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Brown University

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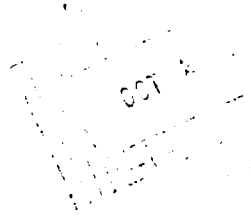

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PREFACE

The Materials Research Laboratory at Brown University is engaged in interdisciplinary research directed toward the solution of problems in various areas of Materials Science.

In this report, Section I - V represent major thrust areas; the remaining sections are less extensive, since they cover either new areas of activity, emerging thrusts with a smaller number of investigators, or derive their principal funding from sources other than the NSF-MRL program.

Although the research summaries in this report are contributions from individual investigators, introductions to the five major thrust area summaries have been provided by investigators who during the reporting period assumed the functions of coordinators of that thrust area. These are: Microscopic and Macroscopic Dynamic Plasticity - R. J. Clifton, Fracture of Solids - J. R. Rice, Inorganic Glasses - W. M. Risen, Jr., Chemisorption on Metallic Surfaces - P. J. Estrup and Chalcogenide Materials - A. Wold.

Since many of the research areas are interrelated, cross references have been made when the work might with equal justice have been placed in two or more different sections.

The Largest single source of support of this Laboratory is the Materials Science Branch of the National Science Foundation. Substantial support also came from seventeen other agencies, including the Advanced Research Projects Agency and of course Brown University.

The Materials Research Laboratory at Brown University is administered technically by a Director, Associate Director and a committee composed of faculty members in representative areas of materials science.

The present appointees are:

INTRODUCTION

Microscopic and Macroscopic Dynamic Plasticity

Progress has been made in both the technical and organizational aspects of the work in Dynamic Plasticity. On the organizational side, bi-weekly discussion meetings were established in order to facilitate the flow of information between investigators working in this field and to make plans for future research that would take maximum advantage of the available capabilities. A decision was made to work jointly on the intrinsic resistance of a lattice to the motion of dislocations. Experiments were initiated to study intrinsic resistance in a common material (LiF) by means of ultrasonic attenuation and plate impact. The change in ultrasonic attenuation due to the presence of a dynamic bias stress was investigated. Tentative conclusions based on the information obtained so far indicate general agreement at low temperatures with results of a completed study for NaCl crystals. Further work on LiF at room temperature and above is required. Progress in the development of a capability for conducting plate impact experiments in which a crystal is subject to a single stress pulse with a duration of .05-.2 microseconds is reported in the summary on Plate-Impact Exerpeiments. Computer simulation of the interaction of high speed dislocations with a simple two-dimensional lattice has resulted in the discovery of breakdown of regular dislocation motion as the dislocation velocity approaches the elastic longitudinal wave speed. Breakdown has been shown to lead to the dissociation of dislocations into super-dislocations and dislocations of opposite sign, and to the formation of twins. Also, computer simulation has indicated that for a one-dimensional model of dislocation motion it is possible for dislocations to continue to move when the applied stress is removed. The plate impact experiments are intended to provide information for determining the applicability of the computer simulation results to the behavior of high-speed dislocations in real crystals.

On the scale of continuum descriptions of plastic deformation based on microscale models of slip, the general features of such formulations have been summarized and a computational technique for applying these descriptions has been examined. Plastic wave speed measurements have suggested that plastic deformation takes place over sufficiently long times for the instantaneous response

of a material to be regarded as elastic. Torsion experiments have been used to investigate the temperature dependence of the change in flow stress associated with a marked increase in strain-rate in order to obtain information on the rate controlling process of the thermally activated motion of dislocations past obstacles. Related information for combined stress states has been obtained for tubular specimens subjected to creep and relaxation.

SECTION 1

Individual Contributions

Microscopic and Macroscopic Dynamic Plasticity

Combined Stress Plastic Wave Propagation in Materials Characterized by Self-Consistent Models of Slip

Combined longitudinal and torsional plastic wave propagation experiments on aluminum tubes have yielded wave profiles which differ somewhat from theoretical predictions based on smooth yield surfaces and rate independent flow rules. This investigation has been undertaken to see whether or not some of the discrepancies are eliminated if the theory is based on modelling polycrystalline deformation as resulting from slip on available slip systems in many randomly oriented single crystals which make up the polycrystalline material. The equations governing slip were formulated as a linear programming problem so that algorithms used for such problems could be applied. So far, the previously computed case of simple tension has been re-computed using the new algorithm. The procedure appears to be efficient and will hopefully allow computation of the much more difficult combined stress cases that are required.

Principal Investigator: R. J. Clifton (Engineering)

Personnel: J. Güldenfennig (Engineering)

Supported by the German Academic Exchange Service and Brown University.

Plate-Impact Experiments

Progress has been made on the development of two new types of plate-impact experiments. In one a single crystal is impacted by a thin flyer plate in order to produce a stress pulse with a duration of .05 - .2 microseconds. This short duration pulse will be used to study the nucleation,

multiplication and high velocity motion of dislocations by observing etch pit configurations before and after loading. Longitudinal and transverse momentum traps are used to prevent further loading of the crystal by reflected waves. Preliminary experiments indicate that recovery of LiF crystals subjected to such pulses is possible. Crystals with sufficiently flat and parallel forces have been prepared; however, lapping introduces surface damage which preculdes the observation of dislocations on the crystal forces. Thus, in the first series of experiments the velocity of dislocations will be inferred from the length of slip bands developed in the interior of the crystals. A significant fallout from this work has been the development of a new technique for aligning two nearly parallel reflecting planes separated by a gap of an inch or more. The technique makes use of a precision, partially reflecting prism and an auto-collimator; deviations from parallelity of less than 0.02 milliradians can be detected. This technique was developed in order to make the tilt between the flyer plate and the crystal as small as possible to ensure the generation of one-dimensional plane waves.

The other experiment consists of imposing pressure-shear loading uniformly over the face of a plate and monitoring the normal and transverse components of the motion at its rear surface. Such loading is achieved by impact of a flyer plate and target plate which are parallel, but inclined relative to the axis of the launch tube. These experiments result in stress states which are more varied and more applicable to the study of dynamic plastic flow than those obtained in conventional normal impact experiments. The main new difficulty associated with these experiments is the measurement of the transverse component of the displacement of the target rear surface. A technique based on diffraction of a laser beam by a 50 lines/mm grating copied onto the target plate, and onto a stationary glass slide separated a small distance from the target, has proved to be successful in preliminary experiments on fused quartz plates.

Principal Investigator: R. J. Clifton (Engineering)

Personnel: A. S. Abou-Sayed (Engineering), L. Hermann (Engineering) and P. Kumar (Engineering).

Publications: None

Supported by the National Science Foundation and the United States Air Force Materials Laboratory.

Plastic Wave Speeds

Experiments have been conducted in which a second torsional plastic wave is propagated along a thin-walled tube of an annealled aluminum alloy (3003-H14) which is already being deformed by an earlier torsional plastic wave. The two wave loading is produced by quick release of elastic strain energy stored in a long transmitter bar with the second wave produced by a reflection from a change in cross-section of the transmitter bar. The wave speed of the second wavefront is found to be approximately equal to the elastic shear wave speed. The experimental results are interpreted as evidence that dynamic plastic deformation does not occur instantaneously but takes place over sufficiently long times for the instantaneous response of the material to be regarded as elastic. Because the maximum strain rate in regions through which the second wave propagates is not greater than 25 sec^{-1} and because of uncertainty in determining its arrival time due to the smoothness of the transition, further work is planned to examine more fully the validity of the conclusion regarding the instantaneous response of the material.

Principal Investigator: R. J. Clifton (Engineering)

Personnel: J. Klepaczko (Engineering)

Publications: Klepaczko, J. and Clifton, R. J., "The Propagation of Plastic Wave Fronts in a Plastically Deforming Aluminum Alloy," Brown University Division of Engineering Technical Report No. ARO-D-G182/9, July, 1974.

Supported by the United States Army Research Office, Durham, and the Advance Research Projects Agency.

Asymptotic Analysis of Inelastic Waves

Previously reported work on stress wave propagation in the direction perpendicular to the faces of elastic and visco-elastic bi-laminates was completed.

Asymptotic analysis of one-dimensional waves in rate dependent plastic materials was investigated. The analysis was based on a constitutive equation which neglected strain hardening in order to model metals which are strongly rate sensitive but exhibit relatively little strain hardening, such as α-titanium. The plastic strain-rate was taken to be a sensitive, non-linear function of stress, consistent with experimental results and a deformation mechanism involving thermally activated motion of dislocations past obstacles. A small parameter

was introduced which goes to zero as the strain-rate sensitivity of the flow stress goes to zero. The hope was that for step-loading conditions the small parameter would allow one to identify boundary layers at the loaded end and possibly at the wavefront. If so, then the main features of the wave profiles could be obtained by perturbation techniques. The analysis failed to yield boundary layer solutions so that the hoped for simplification was not obtained.

Principal Investigator: R. J. Clifton (Engineering)

Personnel: C. C. Chen (Engineering)

Publications: Chen, C. C. and Clifton, R. J., "Asymptotic Solutions for Wave Propagation in Elastic and Viscoelastic Composites," to appear in Proceedings of the 14th Midwestern Congress of Applied Mechanics, March, 1975.

Supported by the Advanced Research Projects Agency.

Computer Simulation of Segmented Slip

This research project is concerned with the computer simulation of dislocations moving through a field of randomly dispersed point defects. These point defects themselves have a random dispersion of attractive and repulsive strengths relative to the dislocations. The array of defects is then read by the computer and a straight line dislocation is made to pass up this field until it makes contact with the obstacles. The dislocation then assumes a segmented shape such that it is attached to certain obstacles and runs as straight line segments between them. The stress is increased upon the dislocation and it either bows out between the obstacles or tears away from them, whichever requires the lower applies stress. In this segmented manner the dislocation is made to transverse the entire slip plane.

Simulation has been limited to straight line segments of dislocations and during the past year, work has been concentrated on improving the program so that it can accommodate dislocations which will bow between bending points and which experience a drag force which is related to the dislocation velocity.

The ultimate goal of the research project is to increase the dislocation velocity toward the sound speed and to determine what effects this high velocity will have on the interaction between dislocations and point defects, i.e. the effective kinetic interaction between a dislocation and a point defect.

The computer program at present is capable of providing output in the form of CALCOMP display of the dislocation at any point of quasi-static equilibrium and also displaying these arrays on a cathode ray tube. In the future, efforts will be made to provide outpout in the form of moving pictures of moving dislocations and to allow on-line manipulation of dislocations and point defects.

Principal Investigator: M. H. Richman (Engineering)

Personnel: T. Stryker, Computer Programmer

Publications: None

Supported by the National Science Foundation.

Deflection Bounds for Impulsively Loaded Structures of Plastic Rate Sensitive Material at Finite Deflections

New theorems are derived which give upper bounds on the deflections of an impulsively loaded structure, valid for large deflections and for a wide class of time-dependent inelastic behavior. The concepts of "extremal path" behavior in strain-time space (due to Ponter) are used, to provide unique definitions of strain energy density for specified strain states reached in a specified time from the reference state. These concepts make available the theorem of minimum potential energy, for the path dependent material. Working from this theorem, it is shown that the deflection at a point of the structure is bounded above by the deflection due to a force applied statically, provided the statice load does total work (computed for extremal path behavior) at least as large as the given kinetic energy at the impulsively loaded structure. The theorem is valid for quite general time dependent behavior, but the application is greatly simplified if the behavior is represented by homogeneous viscous forms. It has been shown that this can be realistically done for structural metals with strong plastic rate sensitivity.

Principal Investigator: P. S. Symonds (Engineering)

Personnel: C. T. Chon (Engineering)

Publications: Symonds, P. S., and Chon, C. T., "Bounds td Finite Deflections of Impulsively Loaded Structures with Time Depdendent Plastic Behavior," Int. Jour. Solids & Structures (in press), Presented at 7th U.S. National Congress of Applied Mechanics, June 1974 (Boulder, Colorado)
ONR Report N00014-003/22 December 1973

Supported by the United States Office of Naval Research.

Mode Approximation Techniques for Dynamically Loaded Structures with Rate Dependent Plastic Behavior at Finite Deflections

"Mode approximation" techniques, which furnish estimates of final deflections and deformation times with a measure of "error" of the approximation, have been extended to problems of finite deflections, of the class in which support constraints lead to tensile (strengthening) effects at finite deflections. The approximating mode solution is constructed from a sequence of "instantaneous" mode form solutions, each satisfying the field equations of the structure with nonlinear terms from finite deflections. An iteration is required to obtain each instantaneous mode solution, but this converges rapidly and is know to be unique, in the class of problems considered. The plastic rate-sensitive material behavior is assumed such that stress-strain rate relations can be derived from convex potential functions. Simplicity is gained by using homogeneous forms, which have been shown to be realistic for strongly rate dependant metals, e.g. steel and titanium alloys. The method is evidently valid for more general loading conditions but in the illustrations is applied to impulsive loading at a fully constrained beam model with two lumped masses.

Principal Investigator: P. S. Symonds (Engineering)

Personnel: C. T. Chon (Engineering)

Publications: Symonds, P. S., and Chon, C. T., "Approximation Techniques for Impulsive Loading of Structures on Time-Dependent Plastic Behavior with Finite Deflections," Proc. Conf. Mechanical Properties of Materials at High Rates of Strain, Oxford, April 1974. Conference Series No. 21, Institute of Physics, 1974. pp.299-316.
ONR Report N00014-003/23 March 1974

Supported by the United States Office of Naval Research.

Intrinsic Resistance to Dislocation Motion in LiF between 4.2°K and 300°K

The main features of the present study are as follows:

(i) Attenuation change due to a dynamic bias stress has been measured in the megacycle range for LiF between 4.2°K and 300°K.

(ii) Experimental data at low temperatures show features similar to low temperature in NaCl. This supports the radiation damping model formulated by Hikata and Elbaum.

(iii) Room temperature data in LiF shows marked differences as compa ed to NaCl. This is possibly due to a larger Debye temperature and a larger Peierl's stress for LiF.

(iv) Qualitatively it appears that both viscous and radiation damping may have significant contributions over the frequency ranges considered in the 300°K results. A quantitative separation and estimation of the viscous and radiation damping is not possible at this stage.

(v) Previous studies of dislocation drag in LiF appear to have overestimated viscous damping contributions at room temperature.

Principal Investigator: Y. M. Gupta (Materials Research Laboratory)

Publications: None

Supported by the National Science Foundation.

Dislocation Dynamics

(i) Breakdown: An important and still controversial question concerns the behavior of dislocations when they approach some appropriate sound speed in the material. It assumes particular relevance in conection with the plate impact experiments being conducted as part of the Dynamic Plasticity activity. Our theoretical work here, using both computer simulation and analytical te nniques, has shown that breakdown of regular dislocation motion occurs when the dislocation approaches the relevant sound speed (that of longitudinal waves for edge dislocations, of shear waves for screw dislocations, according to our preliminary results). The breakdown phenomenon

may also be described as the dissociation of the original dislocation into super-dislocations and dislocations of the opposite sign so that the total Burgers vector is conserved. These super-dislocations and opposite-signed dislocations separate under the applied stress and so increase the resulting plastic flow. Dr. Ishioka is examining the possible relationship between breakdown and twinning in crystals.

(ii) No-loss motion: It has been widely assumed that the fact that a moving dislocation is subjected to a periodic Peierls potential inevitably gives rise to radiation losses due to emitted elastic waves. We discovered in the course of our computer simulation studies of high-speed dislocations in the modified Frenkel Kontorowa model that when the applied stress is slowly reduced to zero the dislocation continues to move under no applied stress in a mode of motion which loses no energy even though the Peierls stress is non-zero. Furthermore, we have been able to verify analytically the existence of this no-loss mode of motion.

Principal Investigator: J. H. Weiner (Engineering)

Personnel: Y. Y. Earmee (Engineering) and M. Pear (Engineering)

Publications: Earmme, Y. Y. and Weiner, J. H., "Breakdown Phenomena in High-Speed Dislocations," J. Appl. Phys. 45, 603 (1974)

Weiner, J. H. and Pear, M., "Breakdown in High-Speed Edge Dislocation Motion," Philosophical Magazine, forthcoming.

Earmme, Y. Y. and Weiner, J. H., "Loss-free Dislocation Motion in a Lattice Model, " Phys. Rev. Letters 33, 1550 (1974)

Supported by the Advanced Research Projects Agency, and the National Science Foundation.

Dynamic Properties of Structural Materials

Explosive loading is used to study the dynamic behavior of metals undergoing either plastic deformation or dynamic fracture. Dynamic plastic deformation is achieved using a split-Hopkinson bar in torsion; the load on the specimen is applied in less than 10 microseconds and strain rates

of 500 to 5000 sec^{-1} are attained. The specimens are short so that homogeneous strain conditions are obtained while plastic flow is occurring. Dynamic fracture is performed by propagating a tensile pulse along a pre-cracked bar.

Current research is directed to investigating the following:

(i) the influence of testing temperature and strain rate on dynamic deformation;

(ii) the influence of previous work-hardening and annealing temperature on dynamic deformation;

(iii) the development of a technique for dynamic fracture initiation and the measurement of crack opening displacement during fracture of steel rods and,

(iv) a combined experimental-theoretical investigation whose goal it is to relate the macroscopic behavior of metals to the underlying dislocation behavior.

Under (i) a report has been published on the effects of testing temperature on the static and dynamic stress-strain characteristics of 1100-0 aluminum in torsional loading. These tests employed a tapered split-Hopkinson bar which preserved constant impedance along the bars in spite of the temperature gradients while the specimens were held at temperatures ranging from -180C to 250C. The techniques developed in these experiments are being combined with our ability to impose large increments in strain rate to achieve the goals outlined in (iv) below.

Under (ii), a study of the effect of strain rate and annealing temperature on the torsional flow stress of OFHC copper and tellurium doped copper has been completed. Annealing temperatures were chosen below, above and near the recrystallization temperature for each alloy. The results showed that for OFHC copper the strain rate sensitivity decreased with increasing annealing temperature. The tellurium copper, on the other hand, showed an unusually high strain rate sensitivity near the recrystallization temperature with decreasing sensitivity for specimens annealed at higher or lower temperatures. This phenomenon was attributed to the coalescence of the tellurium into large irregular particles during recrystallization. Our results are to be published in the Journal of Applied Mechanics.

Under (iii), the technique for conducting dynamic fracture experiments on notched 1-inch diameter steel bars while simultaneously recording crack opening displacement as a function of time is nearly fully developed. A machine that produces concentric circumferential fatigue cracks at the root of the notch has been built. An optical extensometer consisting of a fine grid having 33 lines

per mm produced photographically on the loading side of the specimen just ahead of the notch, and a glass slide having a similar grid pattern on it alligned and mounted over the grid on the specimen and extending across the notch to the transmitter side where it is cemented to the specimen. The relative motion of the loading end moving away from the transmitter end during fracture causes an alternating light and dark pattern to be reflected from the grids. This is monitored by a photodiode whose output is recorded on an oscilloscope. An advantage this method has over any other to measure crack opening displacement is that it requires no calibration except for the initial counting of grid lines.

Under (iv), a combined experimental theoretical investigation whose goal is to relate the macroscopic behavior of metals to the underlying dislocation behavior is underway employing the incremental strain-rate apparatus modified for testing specimens at temperature ranging from -180C to 250C. The experiments involve specimens of two FCC metals: 1100-0 aluminum and OFHC copper; and one HCP metal: zinc. The analytical study will attempt to explain the difference between the dynamic and the static flow stress that occurs in a specimen at the instant when the strain rate increment is applied. Since this increment is applied within less than 10 μsecond, two values of flow stress are obtained at one strain for two very different strain rates. The microstructure under these two conditions is substantially the same. As a result, this experiment provides a value of flow stress for each of two very different strain rates on one specimen with a fixed microstructure.

Principal Investigator: J. Duffy (Engineering)

Personnel: J. Klepaczko, Senior Research Fellow in Engineering, Visiting Brown University from the Polish Academy of Sciences, Warsaw, Poland; P. Senseny (Engineering); R. H. Hawley (Engineering).

Publications: Eleiche, A. M. and Duffy, J., "The Effects of Temperature on the Static and Dynamic Stress-Strain Characteristics in Torsion of 1100-0 Aluminum," International Journal of Mechanical Sciences, pp. 85-96, February 1975.

Klapaczko, J. and Duffy, J., "Strain Rate and Temperature Memory Effects for Some Polycrystalline FCC Metals," Mechanical Properties at High Rates of Strain, Proceedings of the Conference on Mechanical Properties of Materials at High Rates of Strain held in Oxford, England, 2-4 April 1974, pp. 91-101.

Duffy, J., "Some Experimental Results in Dynamic Plasticity," Mechanical Properties at High Rates of Strain, Proceedings of the Conference on Mechanical Properties of Materials at High Rates of Strain held in Oxford, England, 2-4 April 1974, pp-72-80.

Klepaczko, J., "Strain Rate Incremental Tests on Copper," Brown University Report GK-40213/6, May 1974.

Senseny, P. E., Richman, M. H. and Duffy, J., "The Influence of Annealing Temperature on the Strain Rate Sensitivity of Copper in Torsion," Brown University Report ARO-D-G182/8 May 1974 to be published in the Journal of Applied Mechanics.

Klepaczko, J., "Thermally Activated Flow and Strain Rate History Effects for Some Polycrystalline FCC Metals," Materials Science and Engineering, vol. 18, March 1975, pp. 121-135.

Klepaczko, J., Frantz, R. A. and Duffy, J., History Effects in Polycrystalline FCC Metals Subjected to Rapid Changes in Strain Rate and Temperature," Technical Report AFML-TR-1/3, December, 1974.

Supported by the Advanced Research Projects Agency, the National Science Foundation, United States Air Force (Wright-Patterson) and the United States Army (ARO-Durham).

X-Ray Topographic and Microscopic Aspects of Plasticity

Direct Observations of Dislocations in Single Crystal Specimens

(i) Plate-Impact

We intend to examine, by means of x-ray topograhy, the dislocation arrangement in LiF crystals before and after loading in the plate impact experiments and to correlate the observations with the information available from etch pit studies. Several topographs of a LiF cyrstal have been recorded using the Lang scanning method; they showed that the available crystal--which was in the irradiated condition--had substantial substructure which would make resolution of individual dislocations difficult. It was concluded that crystals of considerably high perfection must be obtained for this portion of the research program. (This work is in co-operation with P. Kumar and R. J. Clifton).

(ii) Bending

Direct observation of dislocation displacements by etch pit and anomalous transmission x-ray topography in Fe-3pct Si Single crystals loaded in three point bending have been made. Calculations using our previosuly developed computer program show that published assessments of the resolved

shear stress on competing slip systems when both {110} and {112} slip occurs are slightly in error. The direct observations correlate with the calculated resolved shear stresses and show that the introduction of dislocations in B.C.C. material can be controlled when the differences in stress on primary, secondary, and tertiary systems are adjusted by selecting an appropriate orientation and stress tensor. In particular, when the resolved shear stress on the secondary {110} slip systems is reduced to 0.85 of that on the primary {112} systems, slip is confined to the {112} systems. The dislocation motion can then be examined on the single {112} slip system without the complications of interfering slip on the {110} systems. The asymmetry in etch-pit shape provides a simple optical means for determining the actual slip plane and the expected Burgers vectors are confirmed by X-ray diffraction contrast experiments. (This work is with M. C. Narasimhan)

(iii) Grain Boundaries

We have observed both high and low angle grain boundaries in Fe-3pct Si crystals by x-ray anomalous transmission topograhpy. In low angle boundaries images of individual dislocations are often resolvable,which show diffraction contrast effects similar to isolated dislocations not in the boundary. The strain fields associated with such low-angle boundaries are thus directly observable in x-ray topographs. Images of high angle boundaries, on the otherhand, do not show lattice imperfections directly but are determined primarily by the manner in which the boundary misorientation controls the diffraction geometry in the adjacent grains and not by diffraction contrast. Because of this, the boundary orientation within the crystal interior can be determined by an analysis of the geometry of the diffraction conditions for appropriately selected diffracting planes. (This work is with M. C. Narasimhan).

Dislocation Dynamics

(i) Strain-Rate Equation

The dislocation dynamics strain rate equation $\dot{\epsilon} = \rho b v$ has been examined with particular attention to the question of how to deal with the "spurt like" motion of dislocations in which the dislocation velocity is <u>not</u> a continuous function of time. In direct observation experiments the position of a dislocation is recorded at the beginning and end of a <u>finite</u> interval of time. This fact is incorporated in the

strain rate formulas in order to accomodate the situation encountered in direct observation experiments in which discontinuous dislocation velocities are known to occur. This approach will be applied to existing experimental data on direct observation measurements of dislocation velocity and its applications in simulating macroscopic stress-strain curves explored. (This work is in cooperation with R. W. Armstrong, University of Maryland).

(ii) Simulation of Stress-Strain Curves

A computer simulation of stress-strain curves for strain rate change experiments in aluminum has been made using the dislocation dynamics formulation of Hahn. This approach incorporates the strain rate equation, the empirically determined dependence of dislocation density on strain, and the experimental stress-velocity relation of Vreeland. When at a strain of $\dot{\varepsilon} = -.05$, the strain rate is changed from $\dot{\varepsilon} = 10^{-5}$ to $\dot{\varepsilon} = 1{,}000$ sec^{-1}, the simulated stress strain curve can be made to describe most of the features of the experimental data, such as the incremental increase in stress, the yield drop, and the strain interval over which the drop occurs. The interpreation of these results in terms of structural modeling remains to be completed. (This work has been done with J. Klepaczko).

Principal Investigator: B. Roessler (Engineering)

Personnel: Narasimhan, M. C. (Engineering) and W. Oates (Engineering)

Publications: Narasimhan, M. C., Pd.D. thesis, June 1974., "Image Formation in X-Ray Anomalous Transmission Topography and Introduction of Dislocations in Fe-3% Si Single Crystals,".

Roessler, B., and Burns, S. J., "X-Ray Topographic Observations of Dislocation Annealing and Oxidation in Bulk Zinc Crystals," phys. Stat. Sol. (a), 24, 285, (1974)

Supported by the National Science Foundation.

Plasticity Constitutive Equations in Relation to Microscale Deformation Models

A survey chapter has been prepared on work in this area over the last few years, with emphasis on: internal variable models of deformation mechanisms, principally slip, as operative on the microscale; general structural features of macroscopic constitutive laws, including normality rules; and models for the process of averaging single crystalline constitutive behavior and grain misfit effects so as to predict the macroscopic plastic response of polycrystals.

Principal Investigator: J. R. Rice (Engineering)

Personnel: None

Publications: Rice, J. R., "Continuum Mechanics and Thermodynamics of Plasticity in Relation to Microscale Deformation Mechanisms," in Constitutive Equations in Plasticity (ed: Argon, A. S.), MIT Press - in press.

Supported by the United States Atomic Energy Commission.

Combined Creep and Relaxation

Approach: A tubular specimen is subjected to creep in torsion and stress relaxation in tension simultaneously.

Progress: Experimental work on the aluminum alloy has been completed. Creep and recovery in tension and creep under combined tension and torsion have been analized and a constitutive equation to take into account creep and recovery has been characterized.

Principal Investigator: W. N. Findley (Engineering)

Personnel: R. M. Ree (Engineering)
J. S. Y. Lai, Associate Professor, Department of Civil Engineering, University of Utah

Publications: None

Supported by the National Science Foundation.

Dislocation Dynamics

The contribution of dislocations to ultrasonic attenuation in the liquid-helium temperature range has been measured in sodium chloride for the purpose of determining the resistive force acting on dislocations. Use was made of a technique for measuring the ultrasonic attenuation change $\Delta\alpha$ at different frequencies, caused by a bias stress. The predictions of the extensible-string model of dislocations, which account well for the behavior of $\Delta\alpha$ above about $70^{\circ}K$, are not consistent with the observed frequency and amplitude dependence of $\Delta\alpha$ at lower temperatures. A dislocation-drag model based on a radiation-damping mechanism is shown to account for the present results. Furthermore, this mechanism, taken in conjunction with the viscous damping normally assumed for the extensible-string model, also accounts qualitatively for the behavior of dislocation damping at low frequencies (kHz), which shows discrepancies with the string model.

Principal Investigator: C. Elbaum (Physics & Applied Mathematics)

Personnel: A. Hikata (Applied Mathematics)

Publications: Elbaum, C. and Hikata, A., "Dislocation Drag in Sodium Chloride at Low Temperature-A Radiation-Damping Model," Phys. Rev. 9, 4529 (1974).

Supported by the National Science Foundation, the Advanced Research Projects Agency and the Office of Naval Research.

High Speed Dislocations

Recent development in the lattice theory of dislocations have reopened the question of what happens to a dislocation which moves with a velocity which approaches the sound velocity. Use of an elastic continuum approach to the problem leads only to a Lorenz contraction; however, when the discreteness of the crystal lattice is taken into account the displacement field of a fast moving dislocation is expected to be very different from the static case, because of the excitation of waves. The large stress field of these waves gives rise to new phenomena.

In the present work, use was made of a simple lattice model to calculate the stress field around a high speed dislocation. On the basis of the results, a new model of twining was proposed. This may be regarded as a kind of "breakdown" which was discovered by Earmme and Weiner (Phys. Rev. Letters 31, 1055 (1973) and J. Appl. Phys. 45, 603 (1974).

Principal Investigator: J. H. Weiner (Engineering)

Personnel: S. Ishioka (Materials Research Laboratory)

Publications: Ishioka, S., "Stress Field around a High Speed Screw Dislocation," J. Phys. Chem. Solids, in press.

Summaries of Other Related Work

Crack Propagation - J.H. Weiner (Engineering) - See Section 2

X-Ray Topography and Stress Corrosion - B. Roessler (Engineering) and D.H. Avery (Engineering) - See Section 2

Heat Pulses and Phonon Transport in Solids - C. Elbaum (Physics and Applied Mathematics) - See Section 8

INTRODUCTION

Fracture of Solids

Studies on the fracture of solids continue to encompass phenomena over a range of size scales, from atomistic to microstructural to continuum. Recently completed work has focused on fracture processes at a macroscopic crack tip. This includes the interpretation of macroscale crack growth parameters (e.g., stress intensity factor, J-integral) in terms of elastic-plastic stress field studies and of models for processes of microcrack nucleation and growth from the failure of precipitates and second phase particles. The studies have involved fractures in steels initiated on the microscale both as cleavage and as ductile rupture. Effects of neutron irradiation have been examined in the former case and very high loading rates, generated by stress waves, are being studied for the inception or fracture in steels with significant rate dependence.

Sensitive instrumentaion procedures, based on elastic compliance measurements, have been developed to monitor small amounts of crack growth. The method is accurate to less than 5 μm change in crack length and leads to significantly more precise descriptions of the inception of crack growth, and of stable growth, than previously available. The method holds promise also for the accurate infermence of crack tip processes in other circumstances, e.g. fatigue and stress-corrosion.

Studies of crack growth in idealized lattice models have led to new perspectives on the stability of the atomistically sharp crack configuration and on mechanisms of dislocation generation in tip blunting reactions. Other recent studies, directed to basic fracture mechanisms, include the modelling of diffusive processes of cavity growth under stress at elevated temperature and x-ray topographic observations of metal surface reactions in an oxidizing environment.

Fracture dynamics is being studied in connection with stress analysis for wave-like loadings on cracks, models of running ductile fractures, and observations of stress wave patterns caused by propagating cracks in brittle solids. Other studies include crack growth in composites, failure processes in fluid-infiltrated porous media, especially fissured rocks, finite-element developments for fracture analysis, and formulations of the inception of rupture in terms of the localization of deformation into a shear band.

SECTION 2

Individual Contributions

Fracture of Solids

A Combined Macroscopic and Microscopic Approach to the Fracture of Metals

The problem of interpreting the macroscopic toughness parameters in terms of the deformation and fracture processes at a macroscopic crack is being actively pursued in two directions:

(i) a recently developed incremental finite-element program for problems of arbitrarily large plastic-elastic deformations has been applied successfully to the first of a series of accurate analyses of large deformation processes in the crack tip region, and

(ii) studies of the microscale mechanisms of cleavage initiated rupture at the crack tip in irradiated pressure vessel steel and in spheroidized carbon steels continue to justify the previously stated fracture propagation criteria, namely that a critical local stress level must be achieved in front of the crack and this level must prevail over a significant microstructural size scale.

Work is continuing as well on models for ductile rupture by nucleation and growth of cavities and on particle strengthening of steels. A new study was inititated on diffusive mechanisms of crack growth along grain boundaries at elevated temperatures, with interesting results indicating that the crack growth is limited not by the time-limiting factor in rupture but by the critical stress conditions at the crack tip as affected by the time-dependent overall deformation.

Principal Investigators: J. Gurland (Engineering)
J. R. Rice (Engineering)

Personnel: L. Anand, J. Chvanl, A. L. Gurson, J. Pickens, S. P. Rawal (Engineering)

Publications: Rice, J. R., "Mechanics Aspects of Stress Corrosion Cracking and Hydrogen Embrittlement," to be published by the National Association of Corrosion Engineers, Houston, in proceedings of the International Conference on Stress corrosion Cracking and Hydrogen Embrittlement of Iron Base Alloys, at Firminy, France.

Jindal, P. C. and Gurland, J., "Relation of Hardness and Microstructure of Tempered and Spheroidized Carbon Steels," to be published in Metallurgical Transactions, ASM-AIME.

Rice, J. R., "Continum Mechanics and Thermodynamics of Plasticity in Relation to Microscale Deformation Mechanisms," to be published as Chapter 2 of Constitutive Equations in Plasticity (edited by A. S. Argon), M.I.T. Press.

Supported by the United States Atomic Energy Commission.

Crack Propagation

We have completed some computer simulation studies of a two-dimensional crystal model which permits both crack propagation and dislocation generation. It is a generalization of a model studied analytically by Sanders which permitted only crack extension. The inclusion of the possibility of plastic flow through dislocation generation and propagation introduces interesting new features into its exhibited behavior:

(i) Depending on the values of the model parameters, it behaves at zero temperature in either a brittle manner, in which a pre-existing crack extends under low applied stress with no dislocation generation, or in a ductile manner, in which a crack does not extend but is blunted by dislocation generation from its tip.

(ii) In Sanders' elastic model steady subsonic crack velocities are not possible since the expanding elliptical shape of a finite crack leads to an ever-increasing stress concentration at the tip of the crack which accelerates the crack until it reaches sonic speed. In the present model, however, plastic flow produces a polygonal crack shape with flat central faces and a tip angle which remains reasonably constant during crack extension. Steady subsonic velocities are observed and this terminal velocity is found to be stress-dependent. In agreement with the analytical result of Sanders for the elastic model, supersonic crack speeds have been observed at very high stress levels in the

present model as well.

(iii) It is possible to simulate the effect of temperature in the model by selected random initial atomic velocities. For some model parameters it is found that the effect of temperature on the average crack velocity is small, although thermal motion introduces scatter into the time intervals between successive bond ruptures.

(iv) For other model parameters there is some indication of a qualitative change in behavior as the temperature is raised. This may be indicative of a brittle to ductile transition but further work is needed to clarify this phenomenon.

Principal Investigator: J. H. Weiner

Personnel: R. E. Forman (Engineering) and M. Pear (Engineering)

Publications: Weiner, J. H. and Pear, M., "Crack and Dislocation Propagation in an Idealized Crystal Model," submitted to J. Appl. Physics.

Weiner, J. H., and Forman, R. E., "Rate Theory for Solids. IV. Classical Brownian Motion Model," Phys. Rev. B, 10, 315 (1974)

Weiner, J. H. and Forman, R. E., "Rate Theory for Solids. V. Quantum Brownian Motion Model," Phys. Rev. B, 10, 325 (1974)

Supported by the Advanced Research Projects Agency and the National Science Foundation.

Cracks in Fiber-Reinforced Composites

Materials composed of strong fibers embedded in a weaker matrix can be treated theoretically by (i) an idealized theory, in which the fibers are regarded as inextensible and the composite as incompressible in bulk, by (ii) an inextensible theory, in which the condition of bulk incompressibility is not used, and by (iii) elasticity theory, with the fiber extensibility small but not zero. The problem of plane deformation of a cylindrical body with a crack perpendicular to the fibers was examined with each of these three theories. In particular, the energy release rate for the opening mode of crack advance was calculated. It was found that the result given by the simplest idealized theory reamins qualitatively valid in each of the other two theories, with small

quantitative differences depending upon the small compressibility and extensibility allowed by the latter theories. It was suggested that fracture criteria derived by using the idealized theory should be acceptable as approximations in problems too difficult for use of the more refined theories.

The expression for the energy release rate was used to derive the stress intensity factor for a highly anisotropic material. The explicit dependence on both material moduli and geometrical factors was determined. In particular, it was shown that the stress intensity factor does not depend on geometry alone.

Principal Investigator: A. C. Pipkin (Applied Mathematics)

Personnel: V. Sanchez-M. (Engineering)

Publications: Sanchez-M., V., "Plane Cracks in Highly Anistropic Bodies," Doctoral Dissertation, Brown University, 1975.

Supported by the Advanced Research Projects Agency.

X-Ray Topography and Stress Corrosion

The aim of this research is to examine the process of stress corrosion in single crystal titanium by x-ray topographic observations of the surface exposed to the oxidizing environment. Previous studies in zinc single crystals show that the oxidation process at the metal-oxide surface is directly related to the dislocation content of the underlying metal. In particular, the kinetics of the oxidation process appears to be controlled by the availability of vacancy short circuit diffusion paths along dislocations. This technique will now be extended to examine the feasibility of its application to titanium. The direct observation approach, employing x-ray topographic and microscopic observations of a $\{10\bar{1}0\}$ surface of titanium, was begun in April, 1974. Progress so far is limited but consists of the preparation of a single crystal of titanium and the design, based on dynamical x-ray theory, of a suitable specimen for Berg-Barrett topography.

For cobalt radiation, this requires a crystal cut to a $\{10\bar{1}0\}$ surface so that the $\{11\bar{2}2\}$ diffraction plane is available in the Bragg geometry. We plan to establish, first of all, how well the technique works in titanium crystals and then examine the stress corrosion process.

The information from this surface corrosion study will be used to develop a detailed mechanistic model of the interaction of vacancies and a vacancy flux at the tip of a propagating crack, and hence, to contribute to our understanding of the crystallographic aspects of crack propagation in titanium. (This work has been done in cooperation with E. Savage and D. H. Avery).

Principal Investigators: B. Roessler (Engineering) and D. H. Avery (Engineering)

Personnel: W. Oates (Engineering) and E. Savage (Engineering)

Publications: Roessler, B., "A Discussion of the Characterization of Dislocation Loops in Zinc by X-Ray Topography," phys. stat. Sol. (a), 17, K85 (1973).

Roessler, B., and Burns, S. J., "X-Ray Topography Observations of Dislocation Annealing and Oxidation in Bulk Zinc Crystals," phys. stat. sol. (a), 24, 285 (1974).

Supported by the National Science Foundation.

Analysis of Dynamic Fracture

Research has continued in the general area of dynamic crack propagation in several directions, and work has been completed on the following problems:

(i) The stress intensity factor of a half-plane crack extending nonuniformly in a solid subjected to stress wave loading has been determined. The analysis allows for a delay time between the arrival of the loading pulse which may be incident from any direction, and the onset of fast fracture. The dependence of the delay time on the pulse intensity and on the angle of incidence were calculated on the basis of an energy balance.

(ii) Because crack propagation is an energy absorbing process, the standard energy-based elasto-dynamic uniqueness theorem does not apply for running crack solutions. Based on the universal spatial dependence of the near tip elastic field and the positiveness of the dynamic energy release rate, modifications of the uniqueness theorem have been made which extend its range of applicability to include running crack solutions.

(iii) A one-dimensional model for the steady-state propagation of a ductile crack in an initially pressurized pipeline has been developed. The pipe has been modeled as a rigid-prefectly plastic thin shell, and a Dugdale zone of localized yielding has been assumed to represent separation of material. By means of this model, the required decay length of the residual internal pressure distribution necessary to drive the crack has been estimated.

Principal Investigator: L. B. Freund (Engineering)

Personnel: None

Publications: Freund, L. B., "Crack Propagation in an Elastic Solid Subjected to General Loading IV," J. Mech. Phys. Solids 22 (1974) pp. 137-146.

Freund, L. B. and Clifton, R. J., "On the Uniqueness of Plane Elastodynamic Solutions for Running Cracks," J. Elasticity 4 (1974) pp. 293-299.

Freund, L. B., Parks, D. M. and Rice, J. R., "Running Ductile Fracture in a Pressurized Line Pipe," ASTM STP (to appear).

Supported by the National Science Foundation and the Advanced Research Projects Agency.

Fracture of Solids

During the past year a number of important advances have been made in obtaining a better understanding of the phenomenon of brittle fracture in elastic solids. In particular an analysis of the phenomenon of the fracture of glass beams under conditions of pure flexure has been carried out and the experimental results which have been observed have been explained in terms of the outgoing and reflected stress waves generated by the fracture process. It has been shown that the fracture generally starts at a flaw on the edge of the beam which is under tension and then rapidly approaches the median axis (which was initially the neutral axis) this axis is crossed by the fracture and in a few microseconds the fracture has penetrated 70% of the cross-section of the beam. The speed of fracture propagation then decreases rapidly but the fracture continues to propagate and eventually when about 90% of the cross-section has been traversed, the fracture speed becomes very slow indeed

and on a microsecond time scale the process seems to have come to a stop. Generally at this stage the compression pulses generated by the fracture which have been travelling in an axial direction along the length of the beam return as reflected pulses of tension and these reflected pulses set up a stress field around the fracture which results in the specimen fracturing completely. The completion of fracture can be delayed very considerably by employing very long beams and even more so by cementing steel rods onto their ends, since the main reflected pulses then become ones of compression rather than of tension. By this means fracture times up to seven or eight hundred microseconds have been achieved. This compares with a total fracture time of about 6 microseconds for a similar glass beam under conditions of pure tension.

The history of the fracture process has been studied directly by taking high-speed photographs of the crack growth and at the same time the stress fields accompanying fracture propagation have been studied photoelastically by taking high-speed photographs with the specimen between a circular polarizer and a circular analyzer.

Indirect evidence of the nature of the crack growth has been obtained by recording the dynamic strains with strain gages mounted opposite the point of fracture initiation and at various distances along the beam.

The proposed interpretations of the observed phenomena were as follows: the outgoing cylindrical wave from the crack tip results in a tensile wave propagating out from it, this relieves the compression ahead of the crack tip and enables the fracture to grow, this in turn results in further wavelets being propagated which further relieve the previously compressed region. This process becomes progressively slower since the fracture is entering material which was initially under higher and higher compressive stress and after it has travelled through about half of what was originally the region of compression very little further progress is made, until relieving reflected tensile pulses arrive from the free ends of the beam.

Two other phenomena of interest have emerged from this work, one of these is related to the geometry of fracture propagation. It has been found that when glass breaks under very high applied stress the fracture shows a very definite tendency to bifurcate. This phenomenon of unstable fracture propagation in intense stress fields has been observed earlier, and has been discussed by a number of workers starting with Yoffe (1951). In the present work this type of instability was often observed, but even when a large initial flaw has been present and the fractures propagate in a straight line across the specimen, there was a considerable tendency

for the fracture direction to turn through 90° just before breaking was completed. It is thought that this phenomenon is associated with the reflection of the outgoing cylinrical stress pulse from the crack tip at the bottom free surface of the beam.

Principal Investigator: H. Kolsky (Applied Mathematics)

Personnel: V. Kinra (Engineering) and R. Stanton (Applied Mathematics)

Publications: Proceedings of an international conference on Dynamic Crack Propagation, Ed. George C. Sih, Noordhoff International Publishing, Leyden, 1973, "Recent work on the relations between stress pulses and fracture," H. Kolsky, pp. 399-414.

Kolsky, H., "Wave Propagation Effects and Fracture," In Mechanical Properties at High Rates of Strain, Inst. of Physics, 1975, pp. 199-214.

This work was supported by the National Science Foundation and the Advanced Research Projects Agency.

Diffusive Mechanisms of Elevated Temperature Cavity Growth

The existing theoretical framework for diffusive intergranular creep cavity growth seems to be based mainly on quasi-equilibrium and quasi-steady-state models. Typically, the cavity surface shape is taken as spherical and the stress distribution on the grain interface ahead of it is taken to have its fully relaxed form, so that the adjacent grains move apart as rigid bodies while material from the cavity wall is added to the interface.

This study has involved a fuller modelling of the non-equilibrium aspects of the process, starting with the extreme case of rapid diffusive growth, so that the cavity has a long crack-like shape that can be determined in terms of its speed of spreading and the equations of surface diffusion. Two corresponding limiting cases have been examined for the response of the neighboring grains. The first the case in which adjacent sources of matter (e.g., nearby cavities) are sufficiently close at hand that the relaxed stress distribution prevails along the interface and the adjacent grains separate as rigid bodies. In this case a relation between applied stress and crack speed, V, of the form $\sigma = \alpha V^{1/3} + \beta V^{2/3}$ is found where α, β vary with the diffusive material properties, with the cavity size, and (inversely) with the spacing. By contrast to the corresponding formula based on the assumption of an equilibrium cavity shape,

there is no cut-off stress and a different variation of growth speed with stress at large stress.

The second limiting case imagines the complete absence of neighboring matter sources or sinks. Mathematically, the problem is formulated as a narrow cavity along an infinite grain boundary, and the accomodation of diffusive matter addition to the interface occurs by elastic deformation of the adjacent grains. Growth by this mechanism is found to be possible only at load levels above a critical value, which is approximately 1.7 times the Griffith fracture load for the corresponding problem of an atomistically sharp interfacial crack. Further, the cavity spreading speed increases very rapidly with applied load above the critical level, so that it constitutes an effective cut-off above which rapid diffusive rupture can be considered to ensue.

Principal Investigator: J. R. Rice (Engineering)

Personnel: T. J. Chuang (Engineering)

Publications: Chuang, T-J., and Rice, J. R., "The Shape of Intergranular Creep Cracks Growing by Surface Diffusion," Acta Met., 21, 1973, pp. 1625-1628.

Chuang, T-J., "Models of Intergranular Creep Crack Growth by Coupled Crack Surface and Grain Boundary Diffusion," Ph.D. Thesis, Brown University, Nov. 1974.

Supported by the United States Atomic Energy Commission.

Finite-Element Computational Methods in Plasticity and Fracture Mechanics

Finite-element numerical stress analysis methods are useful adjuncts to studies of plasticity and fracture, especially for cases involving crack-like defects with strongly non-uniform deformation fields near their tips. Indeed, studies of this kind have led to some recent advances in the finite element method, as reported here.

A source of significant error in the numerical estimate of incremental stiffness of fully plastic bodies, including those with plane-strain or three-dimensional constraint typical of some pre-cracked fracture test specimens, has been traced to the propagation of artificial constraints through certain finite-element meshes when these are deformed in a near-incompressible fashion. Criteria for the identification of suitable finite element meshes, free of such propagating constraints,

have been established and some acceptable element designs identified. In addition, a new variational formulation of the incremental plasticity equations has been given, in which the dilational part of the constitutive relation is enforced in a Lagrange multiplyer sense; this leads to a convenient finite element formulation, from which the unknown multiplyers can be eliminated apriori, and which is free of the artificial constraint.

In addition, a simple but rigorous elastic-plastic finite-element formulation has been developed that accounts properly for arbitrarily large geometry changes in deformation and for the occurence of stress levels of magnitude comparable to incremental moduli. This is simplest to utilize in cases for which isotropic strain hardening can be assumed, and it is developed in such a way that existing finite-element programs for "small strain" elastic-plastic analysis can readily be extended along similar lines to the finite deformation context. The program has been tested successfully on a problem of plastic bifurcation, and is being employed to study the finite plastic opening and strain distribution near an initially sharp crack in a ductile material.

Principal Investigator: J. R. Rice (Engineering)

Personnel: R. McMeeking (Engineering) and D. M. Parks (Engineering)

Publications: Nagtegaal, J. C., Parks, D. M., and Rice, J. R., "On Numerically Accurate Finite Element Solutions in the Fully Plastic Range," Computer Meth. Appl. Mech. and Engr., 4, 1974, pp. 153-177.

Supported by the United States Energy Commission and the National Aeronautics and Space Administration.

Models for the Inception and Growth of Shear Rupture Zones

In the absence of macroscopic flaws, the inception of rupture in materials of some ductility frequently takes the form of a localization of essentially homogeneous deformation into a narrow shear band. Indeed, phenomena of deformation localization are widely observed in the mechanics of materials, and include the formation of ductile shear rupture surfaces in metals, owing to unstable void nucleation and growth and, possibly, to the loss of hardening in dynamic recovery at large strains; also, similar localizations are observed in

densely packed, or overconsolidated, soils and in fissured rock masses deformed under predominantly compressive stresses.

Studies during this reporting period include the general formulation of a criterion for localization of deformation, viewing it as an instability discernible in terms of properly formulated constitutive laws describing inelastic behavior of the material at hand. The framework has been implemented through separate studies on the inception of void-growth ruptures in ductile metals, and on processes of shear faulting in soils and rocks.

The formulation of conditions for localization shows a strong dependence on the nature of the pre-instability deformation; e.g., critical conditions are met far earlier with plane strain deformation than with axi-symmetric compression or extension. Also, results are very much dependent on whether, in plasticity terminolgy, a "vertex" develops at the current stress point on subsequent yield surfaces in stress space. The simpler classical constitutive theories for plasticity involve smooth yield surfaces, whereas those based on more direct physical models of slip processes (either at the crystalline slip level in metals, or frictionally on fissure surfaces in rock masses) seem uniformly to lead to the expectation of yield vertices. The matter is important because conditions for bifurcation in the form of a shear localization entail the response of the material to deformation increments differing in "direction" from that for the pre-instability deformation; the response to deformations that are orthogonal, in a certain sense, to the previous deformation is governed by elastic moduli in the simple classical theories, but by considerably reduced elastic-plastic moduli in the presence of a vertex. The reduced moduli mean that bifurcation conditions are met at a correspondingly earlier stage in the deformation.

The more detailed studies of the inception of ductile rupture in metals are aimed at the formulation of macroscopic, dilational constitutive laws for a void-containing plastic materials. Most work to date has been directed to modelling the ductile growth of existing voids in the presence of variable stress triaxiality, although the incorporation of void nucleation from inclusions has recently been undertaken. Instability conditions, in the form of the macroscopic hardening rate falling to zero, are met when the incremental softening by porosity increase, due to void nucleation and growth, is just adequate to balance the incremental hardening of the surrounding matrix.

Studies on the geological materials have emphasized the role of frictional conditions at fissures in determing "plastic" response, and have been concerned also with a proper formulation of the role of pore-fluid pressures

in inelastic constitutive descriptions. Since fissured rock and heavily consolidated soils tend to dilate as they are deformed in shear, rapid shearing (by comparison to pore-fluid diffusion times) induces suctions in the pore fluid and thus serves to "dilatantly harden" the material over the resistance to deformation that it would show under drained conditions. Such hardening deformation has been shown, however, to undergo an internal diffusive instability when conditions are met for which the underlying drained deformation has reached the condition for shear localization.

Principal Investigator: J. R. Rice (Engineering)

Personnel: A. E. Gurson (Engineering), M. P. Cleary (Engineering), and J. W. Rudnicki (Engineering)

Publications: Rice, J. R., "The Initiation and Growth of Shear Bands," in Plasticity and Soil Mechanics (ed., Palmer, A. C.), Cambridge Univ. Engineering Dept., Cambridge, 1973, pp. 263-274.

Rice, J. R., "On the Stability of Dilatant Hardening for Saturated Rock Masses," J. Geophys. Res. - in press.

Cleary, M. P., "Continously Distributed Dislocation Model for Shear Bands in Geological Materials," Int. J. Numerical Meth. Engr. - in press.

Rudnicki, J. W., and Rice, J. R., "Conditions for the Localization of Deformation in Pressure - Sensitive Dilatant Materials," J. Mech. Phys. Solids - in press.

Supported by the United States Atomic Energy Commission, and the National Science Foundation.

Mechanics of Crack Growth in Ductile Metals

The general aims are to develop quantitative criteria for crack growth in ductile structural metals, especially under conditions for which large scale plastic yielding accompanies fracture, and to relate macroscopic cracking resistance (toughness) parameters to the microscale processes of cracking such as cleavage and rupture.

Work in the present reporting period has included the development of instrumentation to detect small amounts of stable crack growth in pre-fatique-cracked fracture

test specimens. This relies on accurate measurement of the change in overall elastic compliance, as detected for small increments of elastic unloading, and presently gives accuracy of better than 5μm of crack growth. The method is being used to study the very early stages of stable crack growth, as correlated in terms of the J Integral, and seems to make possible a considerably more refined description of initiation and early growth than has previously been possible. Coordinated experiments involve the wedging open of a cracked specimen, and filling of the crack space with epoxy, under conditions of negligible plastic unloading at the tip. Sectioning studies have thereby been initiated which allow an examination of the crack tip and rupture mechanism topography at the inception of growth and after variable amounts of stable growth. Studies of this type are being continued for several structural metals, with an aim toward the delineation of crack growth processes in the presence of a variety of microstructures and rupture mechanisms. It is also worth noting that these same experimental techniques may be applied to other modes of cracking, such as fatigue, creep, etc., as well as these monotonic loading tests.

Elastic-plastic stress analyses of crack tip regions, by the finite-element method, have been continued with special emphasis on the delination of the effects of different strain hardening behaviors, and also on the adaptation of a recently formulated finite deformation program to the treatment of the large plastic straining involved in crack tip blunting. Here the emphasis is on obtaining accurate descriptions of the deformation field at distances from the tip comparable in size to its plastic opening; this has been shown in previous work to be the size scale in the material where progressive void rupture processes coalesce to a macroscopic fracture.

In addition to providing a description of the stress state very near a crack tip and of its alteration by finite deformation effects, the numerical results are also to be used in conjunction with void nucleation (typically by second phase particle failure) and enlargement models to study the angular dependence of progressive void growth near the tip. This may contribute to an understanding of the frequently observed tendency for rupture to initiate on surfaces at an angle with the main fracture, and to grow on a roughened or, sometimes, zig-zag-like surface, even when the macroscopic surface of fracture is essentially flat.

Finally, previous analytical results on crack tip stress fields have been used to explain the results of neutron irradiation on the lower temperature cleavage fracture of a nuclear pressure vessel steel. The assumption is that the local stress necessary to nucleate cleavage microcracks from inclusions is not altered by the irradiation; rather, the effect is only to alter the yield strength and hardening behavior of the material, and hence the distribution of stresses in the plastic region ahead of a crack for some given level of applied loading. The resulting predictions of irradiation effects on fracture, in terms of measured flow properties and the elastic-plastic crack tip stress analyses, agree well with available experimental data.

Principal Investigators: P. C. Paris (Engineering) and J. R. Rice (Engineering).

Personnel: L. Herrmann (Engineering), L. Van Swam (Engineering), D. M. Tracey (Engineering), R. McMeeking (Engineering), and D. M. Parks (Engineering).

Publications: Rice, J. R., "Limitations to the Small Scale Yielding Approximation to Crack Tip Plasticity," J. Mech. Phys. Solids, 22, 1974, pp. 17-26.

Tracey, D. M., "Finite Element Solution for Crack Tip Behavior in Small Scale Yielding," Trans. ASME, J. Engr. Materials and Tech. - in press.

Parks, D. M., "Interpretation of Irradiation Effects on the Fracture Toughness of a Pressure Vessel Steel in Terms of Crack Tip Stress Analysis," Trans. ASME, J. Engr. Materials and Tech. - in press.

Rice, J. R., "Mechanics Aspects of Stress Corrosion Cracking and Hydrogen Embrittlement," in Proc. Int. Conf. on Stress Corrosion Cracking and Hydrogen Embrittlement of Iron Base Alloys, Nat. Assoc. Corrosion Engrs. - in press.

Clarke, G. A., Andrews, W. R., Paris, P. C., and Schmidt, D. W., "Single Specimen Tests for J_{IC} Determination," ASTM - STP (Proc. 1974 Symp. on Fracture Mech.) - in press.

Argy, G., Paris, P. C., and Shaw, F., "Fatigue Crack Growth and Fracture Toughness of 5083 - 0 Aluminum Alloy," ASTM - STP (Proc. of the Symposium on Properties of Materials for LNG Tankage, May 1974) in press.

Supported by the United States Atomic Energy Commission, the Advanced Research Projects Agency, the National Aeronautics and Space Administration, and the National Science Foundation.

Criteria of Fracture

The following work was done in the program of study of fracture criteria in the region of large plastic strains, but below full plasticity.

(i) The testing of maraging steel specimens, found preferable to the earlier aluminum 2219 specimens, required the design of a bigger 300,000 lb. testing machine. Its construction was completed and tested this year. Special pulling heads were also made.

(ii) Tests were made for selecting the proper degree of hardening of maraging steel so as to achieve a wide range of plastic zone sizes within the limited range of specimen sizes which can be tested in our equipment.

(iii) The present tests are with round bars having a circumferential crack, produced in a special rotating bending fatigue machine. The crack opening displacement is measured up to fracture in four positions around the specimen. A new fifth extensometer was constructed for the measurement of the overall extension of the specimen, as is used in the calculation of the J-integral as a possible criteron of fracture.

(iv) Thirty-three maraging steel specimens of 1-in and 0.5-in O.D., with circumferential cracks were prepared and tested. Crack extension curves, K_{1C} values and J-integral values were calculated at several degrees of hardening.

(v) The results as yet appear inconclusive for the J-integral. With specimens of 0.5-in O.D. the J-integral values are ordered in the expected way for various degrees of material hardness, as also do the crack opening displacements. Yet for the 1-in O.D. the J-integral was found to be larger than for 0.5-in O.D. contrary to expectation.

Principal Investigator: C. Mylonas

Personnel: L. Hermann (Engineering) and J. Tracey (Engineering)

Publications: None

Supported by the Advanced Research Projects Agency and the National Aeronautics and Space Administration.

Influence of Intermediate Principal Stress in Fatigue

In order to determine the effect of the intermediate principal stress on fatigue of an aluminum alloy, thick-walled tubes are subjected to pulsating internal pressure and superimposed axial tension or compression of different magnitudes.

All experiments have been performed, and a report has been prepared.

Principal Investigator: W. N. Findley (Engineering)

Personnel: J. F. Tracy (Engineering)

Publications: Findley, W. N., "An Explanation for Size Effect in Fatigue of Metals," The Institution of Mechanical Engineers, Journal of Mechanical Engineering Science, Vol. 14, No. 6, 1972, pp. 424-425.

Findley, W. N., and Tracy, J. F., "The Effect of the Intermediate Principal Stress on Triaxial Fatigue of 7075-T6 Aluminum Alloy," ASTM Journal of Testing and Evaluation Vol. 1 No. 5. Sept. 1973, pp. 432-434.

Supported by the National Science Foundation.

Creep of Metals under Biaxial Stress

Objective: To investigate the behavior of 304 stainless at elevated temperatures under combined stressing and devlop suitable constitutive equations.

Approach: Experiments are employed in which the temperature and state of combined tension and torsion are altered abruptly according to a planned schedule.

Progress: Apparatus modification required for tests at 1200°F have been made and long-time constant stress tests have been performed at 1100°F and effective stresses of 10, 12.5 and 15 ksi. Apparatus for creep in compression and internal pressure in tubes has been developed.

Cyclic creep tests have been performed following creep for 1000 hr. Yield surface subsequent to creep for 1000 hr. has been explored. A model to describe plasticity, creep and recovery is being investigated.

Principal Investigator: W. N. Findley (Engineering)

Personnel: R. Mark (Engineering) and R. M. Reed (Engineering)

Publications: Findley, W. N., and Mark, R., "Multiaxial Creep Behavior of 304 Stainless Steel," Annual Report No. 1 on Union Carbide Subcontract 3599, October 1972.

Findley, W. N., and Mark, R., "Multiaxial Creep Behavior of 304 Stainless Steel," Annual Report No. 2 on Union Carbide Subcontract 3599, October 1972.

Supported by Union Carbide 3599.

Summaries of Other Related Work

Dynamic Properties of Structural Materials - J. Duffy (Engineering) - See Section 1

X-Ray Topographic and Microscopic Aspects of Plasticity - B. Roessler (Engineering) - See Section 1

Theoretical and Experimental Studies of Thermodynamic, Fluid Dynamic and Metallurgical Phenomena in Electric Discharge Machining - P.D. Richardson (Engineering) and J. Gurland (Engineering) - See Section 6

INTRODUCTION

Inogranic Glasses

Experimental investigations of inorganic glasses and theoretical research on amorphous state materials and new methods for studying their properties, carried out during this period within the Inorganic Glasses Group, are reported.

Structure and bonding in inorganic glasses is a central experimental focus in this research area. These studies include: 1) P. J. Bray's work employing nuclear magnetic resonance studies on binary $Ag_2O-B_2O_3$ systems (^{11}B), and ternary $PbO-B_2O_3-SiO_2$ and $MgO-Na_2O-B_2O_3$ systems (^{207}Pb,^{11}B), 2) P. C. Hess' and M. J. Rutherford's studies of structure-property relations in complex and phase-separated silicate systems, 3) W. Risen's Raman and infrared investigations of ionic phosphate glasses, and J. Tauc's Raman studies of structure in the As_2Se_3 system.

The crystallization and glass transition processes in ionic oxide (Risen) and arsenic chalcogenide (Tauc) systems have been studied by laser Raman techniques. Experimental and theoretical work on electromagnetic properties of glasses has been especially facilitated by the developments in time domain spectroscopy reported by R. H. Cole. Hydrodynamic equations for amorphous, as well as crystalline, solids have been developed in J. H. Gibbs' theoretical studies. These have led to recognition, in the case of glasses, of two diffusive modes interpreted as heat flow and "configurational rearrangement", which are coupled via thermal diffusion of the configuarational rearrangement. Ionic motion, over long or short range, has been related by P. J. Bray to nuclear magnetic resonance line-narrowing for lithium silicate and borate glasses. Cation vibrational information from infrared spectroscopy has been related to activation of ionic motion by W. M. Risen. In each of these, approaches developed for understanding transport behavior of ionic inorganic glasses are reported.

SECTION 3

Individual Contributions

Inorganic Glasses

Trace Element Partitioning Among Coexisting Immiscible Silicate Melts

Experiments were performed to investigate the nature and extent of melt-melt phase separation in the system Fe_2SiO_4-$KAlSi_2O_6$-SiO_2, the only silicate system where super-liquidus immiscibility occurs at low ($\sim$ 1000°C) temperatures. The coexisting immiscible phases correspond to a phase-rich in network forming cations (approximately 75% SiO_2) and a phase poor in network forming cations (approximately 45% SiO_2). The compositions of the coexisting liquids were obtained by electron microprobe analysis. Other elements, in the form of oxides, were added to this system to establish the nature and degree chemical fractionation of these elements between the phase-separated melts. Cations of high field strength such as Mg, Ti, Ca, Fe, P, Yb, La were partitioned into the network-poor melt. Those cations capable of tetrahedral coordination with oxygen (Al) and those needed for charge balance when Al is added (K, Na, Ba) are partitioned into the network-rich melt. Apparently, in the SiO_2-rich polymerized melts, cations of high field strength cannot obtain a coordination polyhedron of oxygen and are thereby partitioned into the SiO_2-poor melt where bridging oxygen species are less abundant. These studies are being continued in order to identify and quantify those factors that control the occurrence of the critical state in silicate liquids and glasses.

Principal Investigator: P. C. Hess (Geological Sciences)

Personnel: M. Wood (Geological Sciences) and F. Ryerson (Geological Sciences)

Publications: Hess, P. C. (in press), "PbO-SiO_2 melts: Structure and Thermodynamic Mixing Properties," Geoch. Cosmo. Acta.

Tewhey, J. D. and Hess, P. C. (1974), "Two Phase Region of SrO-CaO-SiO_2 melts: EOS, " v.55, p. 483, ABS.

Hess, P. C. and Rutherford, M. J., (1974), "Element Fraction Between Immiscible Melts," Fifth Lun. Sci. Conf. p. 328-329.

Rutherford, M. J. and Hess, P. C. (1974), "Experimental Liquid Line of Descent and Liquid Immiscibility for Basalt 70017,". Fifth Lunar Sci. Conf. p 569-584.

Supported by the National Science Foundation.

Composition and Structure of Compex Silicate Glasses

A variety of studies currently in progress are directed at developing a better understanding of the strucute of glasses, and how physical and chemical properties change with variations in the structure. This is being attempted through synthesis and annealing experiments both on single phase and immiscible glasses. A field of immiscibility which occurs in simple metal oxide - SiO_2 systems has and is being studied. A similar field of immiscibility is present in complex multicomponent systems analogous to some of those found naturally. The paths followed by natural liquids in reaching and penetrating this field has been determined experimentally. They involve a gradual increase in the network breaking cations Fe^{++} and K^{+} with essentially no change in the amount of SiO_2 and Al_2O_3. Experiments are now in progress to determine the extent of the immiscibility field, the structure of these two phases, and the diffusivity of ions in these glasses. Electron microprobe and optical studies suggest that structurally the two glasses resemble the two major phases that crystallize in this system. One of these minerals is a framework silicate, the other is a chain silicate.

In related studies, binary and multicomponent glasses have been synthesized and analysed under various operating conditions on the electron microprobe. One objective of this investigation is to establish standards for quantitative glass analyses, and also the optimum microprobe operating conditions for these analyses. This has been completed, but work in continuing on the problem of why some glasses undergo chemical change under the electron beam. A second objective is to determine bond length changes and hence continuous and discontinuous structural changes in the glases by measuring changes in the x-ray spectra.

Principal Investigator: M. J. Rutherford (Geological Sciences)

Personnel: R. Guillemette (Geological Sciences) and
H. Tuchfield (Geological Sciences)

Publications: Rutherford, M. J., Hess, P. C. and Daniel, G., 1974, "Experimental Liquid Line of Descent and Liquid Immiscibility for Basalt 10017," Proc. 5th Lunar Sci. Conf., Geoch. Cosmochim. Acta, Supp. 5, Vol. 1. pp. 569-583.

Rutherford, M. J. and Hess, P. C., 1975, "The Origin of Lunar Granites as Immiscible Liquids," Lunar Sci. 6 (in press).

Supported by the National Science Foundation and the National Aeronautics and Space Administration.

Nuclear Magnetic Resonance Studies of the Structure of Glasses

B^{11} Nuclear Magnetic Resonance (NMR) has been used to study the structure of glasses and crystalline compounds in the system Ag_2O-B_2O_3. The data yield the following information about the structure of these materials:

(i) The fraction N_4 of boron atoms in BO_4 units in the glasses is given by x/100-x up to at least 30 molar % Ag_2O, where x is the molar % of Ag_2O.

(ii) The silver tetraborate ($Ag_2O.4B_2O_3$) a diborate ($Ag_2O.2B_2O_3$) compounds are isostructural to the corresponding alkali borate crystalline compounds.

(iii) NMR data for these two compounds are also identical to those obtained for the corresponding glasses. Therefore, the silver borate glasses are best described in terms of the structural model proposed by Krogh-Moe, in which a glass is viewed as a random network of structural groupings that occur in crystalline compounds of the system.

An equation has been developed for NMR motional narrowing in solids which is based on the concept of two possible states for each ion: excited and nonexcited. The excited state corresponds to thermal activation. The equation can be obtained from the Bloch equations. It does not explicitly involve a jumping frequency or correlation time, and results calculated using the equation should not be distorted by a distribution of correlation times. The derivation of the equation does not required knowledge of an auto-correlation factor or of the frequency spectrum of microscopically varying local fields. It provides a relation for NMR line

width vs temperature which reduces to the Redfield equation in the extreme high-temperature range, but which also yields apparently meaningful results throughout the entire temperature range of motional narrowing. The utility of the equation in handling experimental data has been demonstrated with examples of motional narrowing in crystals and glasses of the systems Li_2O-B_2O_3 and Li_2O-SiO_2. The results provide a guideline for determining the nature of the motion (long-range or short-range) causing narrowing of the NMR line.

^{207}Pb NMR spectra for seven lead-containing compounds have been obtained in the absorption mode. The lineshapes, linewidths, and chemical shifts have been analyzed and the results correlated with the bonding character, site symmetry, and relaxation processes of the lead atoms. It is found that the Pb^{207} NMR spectra yield useful data on the nature of the lead-oxygen bonds and the symmetries of the lead sites. The anisotropic chemical shifts for the lead atoms in various sites are of particular help in determing the bonding and atomic arrangements. These findings have been employed in analyzing the Pb^{207} NMR spectra for glasses in the ternary system PbO-B_2O_3-SiO_2. The Pb^{207} data, and NMR data for B^{11} in these glasses, permit formulation of a model for the locations and bonding configurations of both boron and lead in these lead borosilicate glasses over the entire glassforming region of composition.

B^{11} Nuclear Magnetic Resonance (NMR) has been used to study glasses in the system MgO-Na_2O-B_2O_3. The fraction N_4 of boron atoms in BO_4 units is analyzed according to a method developed for this system. It is concluded that both MgO and Na_2O behave as network modifiers in the glasses containing less than 0.15 molar fraction of MgO. As the MgO content increases further, some of the MgO enters into formation of the glass network, presumably in the form MgO_4 tetrahedra. A substantial fraction of the BO_3 units in glasses of high Na_2O content have non-bridging oxygens. Previous N_4 data for "CaBAl" glasses have also been analyzed using the new method.

Principal Investigator: P. J. Bray (Physics)

Personnel: G. E. Jellison (Physics), Y. H. Yun (Physics) L. W. Panek (Physics) and K. S. Kim (Physics).

Publications: Bray, P. J., Hendrickson, J. R., "Studies of Local and Long-Range Motions of Alkali Ions in Glasses," J. Non-Crystalline Solids 14, 300-301 (1974). (Extended abstract).

Kim, K. S. and Bray, P. J., "NMR in Lead-Containing Compounds," J. Magnetic Resonance 16, 334-338 (1974)

Kim, K. S. and Bray, P. J., "B^{11} Nuclear Magnetic Resonance Studies of the System Ag_2O-B_2O_3", J. of Non-Metals 2, 95-101 (1974).

Bray, P. J., "Trends for Application of NMR for Structural Analysis of Glasses," Wissentschaftliche Zeitschrift der Friederich - Schiller - Universitat, Mathematish - Naturwissenschaftliche Reihe, Heft 2, pages 267-270 (1974). (Proceedings of the "Jena Conversations on Glass," 12-14 June 1973, Jena, DDR.)

Hendrickson, J. R. and Bray, P. J., "A Phenomenological Equation for NMR Motional Narrowing in Solids," J. Magnetic Resonance 9, 341-357 (1973).

Supported by the National Science Foundation, the Advanced Research Projects Agency and an Innotech Glass Research Fellowship.

Raman Studies of the Crystallization of As_2Se_3

An important group of amorphous semiconductors can be prepared in the bulk form by quenching the liquid. Recently, we have reported Raman studies on a typical representative of this group As_2S_3 in which we related the vibrational specta of the amorphous solid with those of the liquid and suggested a model for the structural changes[1]. When we extended this work to As_2Se_3 we observed crystallization between the glass-transition temperature T_g and the melting point T_m. We have found that the rate of crystallization can be adjusted for easy observation by Raman Spectroscopy by a proper choice of temperature, laser beam intensity and sample history. The method is very suitable for studying the influence of these factors on the crystallization since we can follow the process continuously.

Raman spectra of As_2Se_3 were measured as a function of time during photocatalyzed crystallization. From this

[1]E. Finkman, A. P. DeFonzo and J. Tauc, Raman Spectra of Liquid As_2S_3 and Their Temperature Dependence. Amorphous and Liquid Semiconductors, (Editors J. Stuke and W. Brenig), Taylor and Francis, London, 1974, p. 1275.

study we could draw some conclusions about the crystallization process. The development of the crystalline spectra from the amorphous spectra showed in a particularly dramatic way the relationship between these two spectra.

This work is part of an extended study on the changes of the vibrational spectra of amorphous solids during the glass-transition aimed at the understanding of the structural differences between the crystalline, glassy and liquid states.

Principal Investigator: J. Tauc (Engineering & Physics)

Personnel: E. Finkman (Engineering), and A. P. DeFonzo (Physics)

Publications: Finkman, E., DeFonzo, A. P. and Tauc, J., "Raman Studies of the Crystallization of As_2Se_3," Proceedings of the 12th International Conference on the Physics of Semiconductors, Stuttgart, Germany, July 1974, p. 1022.

Finkman, E., DeFonzo, A. P., and Tauc, J., "High Temperature Raman Spectra of Amorphous As_2Se_3," Bull. APS 19, 212 (1974)

DeFonzo, A. P., Finkman, E., and Tauc, J., "Raman Spectra of Partially Ordered Liquids," Bull. APS 19, 284 (1974)

Supported by the National Science Foundation.

Ionic Conductivity Activation Energies in Ionic Oxide Glasses from Spectoscopic Data

The observation of cation-motion vibrational bands in the far infrared spectra of ionic oxide glasses of the form $[(M_2O)_xA_nO_m](gl)$ provides a measure of the cation-site vibrational frequency from which the activation energy for ionic conductance has been calculated through an approach developed in this work, for a variety of metaphosphate and silicate glasses. This band encompasses the cation-vibrational modes which are thermally excited to high ($n>>1$) levels in the activation to ion transport, and an analysis of the excitation leads to expression of E_a as a function of ν (band frequency) ℓ (the ionic displacement) and μ (effective mass). Two results are of primary interest; first, the values of E_a calculated from the spectral observations are in good agreement

with those found by conductance experiments on Li, Na, Rb, Ag glasses of the metaphosphate and several silicate series, and, second, the relationship between ionic displacement distance and "critcal vibrational amplitude" has been established. Evaluation of E_a from spectral data have been made for several related series of glasses.

Principal Investigator: W. M. Risen, Jr. (Chemistry)

Personnel: G. J. Exarhos (Chemistry) and P. J. Miller (Chemistry)

Publications: Exarhos, G. J., Miller, P. J., and Risen, Jr., W. M., "Calculation of Ionic Conductivity Activation Energies in Ionic Oxide Glasses from Spectroscopic Data," Solid State Commun., accepted for publication (1975).

Supported by the National Science Foundation and the United States Office of Naval Research.

Raman Study of Isothermal Devitrification Kinetics of $(NaPO_3)_x$ Glass

A laser Raman spectroscopic method was developed by which the increase in crystallinity of a devitrifying glass can be monitored continously and isothermally at the devitrification temperature, without sample quenching, in a molecularly specific manner that yields high quality kinetic data for the glass-crystal transformation. The transformation $(NaPO_3)_x$ (gl) to $NaPO_3$(cry.) was studied by this method, and the continuous data were fitted, by non-linear least squares analysis to the form $\alpha(t) = 1-\exp(-k_N t^N)$ with sufficient precision to permit optimization with respect to both k_N, the rate constant, and N, the order. Through study of the process at a range of devitrification temperatures,T, where $T > T_g$, the activation parameters were determined, and E_{Nucl} was found equal to E_{crys}, although the rates depend on glass thermal history.

Principal Investigator: W. M. Risen, Jr. (Chemistry)

Personnel: G. J. Exarhos (Chemistry) and A. U. Paeglis (Chemistry)

Publications: Exarhos, G. J. and Risen, Jr., W. M., "Raman Study of Isothermal Devitrification Kinetics of $NaPO_3$ Glass," Journal of the American Ceramic Society 57, 401 (1974).

Supported by the National Science Foundation and the United States Office of Naval Research.

Evaluation of Electromagnetic Properties by Time Domain Spectroscopy

New mathematical analyses have been developed to determine dielectric and conductivity of materials from reflected voltages in coaxial lines observed by methods of time domain reflectometry. These have advantages over steady state methods that data over virtually continuous range of times from 10 picoseconds to 0.1 microseconds are quickly and simply obtained, but previous analyses have been seriously limited by limited range of usefulness in time, complex numerical procedures, or signal/noise problems.

The new methods take exact account of finite reflected wave amplitude with no long time limitations. In the simplest "real time" analysis, dielectric response functions for times greater than 100 picoseconds are obtained by simple numerical integration and convolution of the reflected signal. Tests using a variety of dielectrics with reasonably well known behavior from other methods have confirmed the validity and usefulness of the method.

A complementary more powerful analysis in the "frequency domain" was also developed in the period covered by this summary. Simple numerical Fourier transformations of the reflected voltage-time profile can be used to evaluate complex permittivity up to 3GHz or frequencies such that the sample length does not exceed one-sixth of the electrical wavelength. These procedures have also been tested in subsequent work, and applications to glassy systems are being undertaken.

Principal Investigator: R. H. Cole (Chemistry)

Personnel: None

Publications: Cole, R. H., "Dielectric Response by Real Time Analysis of Time Domain Spectroscopy Data," J. Phys. Chem. 78, 1440 (1974).

Cole, R. H., "Evaluation of Dielectric Permittivity by Time Domain Spectroscopy," J. Phys. Chem. 79, 93 (1975).

(Two full length papers have been submitted to J. Phys. Chem.).

Supported by the National Science Foundation.

Statistical Mechanics of Supercooled Liquids and Glasses

In this work the hydrodynamic equations for both crystalline and amorphous solids have been derived from the connection between hydrodynamic variables (and linearized hydrodynamic modes) and continuous broken symmetries.

A simple fluid has 5 hydrodynamic variables (and modes), one for each conservation law (mass, 3 components of momentum and energy). As pointed out by Martin, Pershan and Parodi a crystal must have 3 additional hydrodynamic variables (and modes) because it does not possess the (threefold) continuous translational invariance of the underlying Hamiltonian of the system. Previous treatments of the hydrodynamics of solids gave only 7 hydrodynamic modes (6 propogating sound modes and one dissipative mode). The additional mode we have found for crystals, which was omitted from these earlier treatments, is associated with vacancy diffusion. Previous treatments of vacancy diffusion failed to recognize its coupling with the other hydrodynamic variables.

The recognition of the necessity of inclusion of vacancy diffusion has led to the identification of two tensor transport coefficients (in addition to the usual viscosity and thermal conductivity). One is associated with the vacancy flux while the other is connected with the cross effect of thermal diffusion of vacancies (or equivalently a heat flow in a vacancy concentration gradient).

The linearized equations have been solved for propagation along the [1 0 0], [1 1 0] and [1 1 1] directions in cubic crystals. For these directions the longitudinal equations are isomorphic with those in a binary mixture when vacancy concentration is identified with the concentration in the mixture. In these cases the identification of the additional mode with vacancy diffusion is most clear. It is suggested that this additional mode should appear in the spectrum of light scattered from such crystals.

With regard to experiments performed in reasonable times, any particular sample of a glass may also be recognized as lacking continuous translational invariance (even though it lacks the geometrical order of a crystal), for the absence of any significant molecular displacements in such times precludes equivalence of different points in the sample even as viewed in time averages taken over

these times. Thus a glass also possesses 8 hydrodynamic modes, as contrasted with the 5 of a fluid. As in the case of a crystal, one of these, a dissipative mode, has previously been missed. An analysis, parallel to that for the crystal has also been carried out for the glass case. For the glass case, however, the concept of "vacancy" defies precise definition. However, the more general (if less convenient for a crystal) concept of local configuration can and has been used instead for the glass case.

The solution to the linearized equations for a glass can be represented in terms of two longitudinal diffusion modes, two longitudinal sound modes and two two-fold degenerate transverse sound modes. The two diffusive modes are interpreted as heat flow and "configuational rearrangement". The two are coupled, however, via a thermal diffusion of the configurational rearrangement.

The spectrum of light scattered from such a system is calculated from these equations. The polarized Rayleigh peak consists of two Lorentzian lines similar to that observed in a binary mixture. The configuarational rearrangement in the glass plays the role of concentration diffusion in the binary mixture. The Brillouin peak has the usual interpretation of a sound propagation mode with an additional attenuation due to the coupling to configurational rearrangement. The transverse sound modes contribute to the depolarized spectrum.

Principal Investigator: J. H. Gibbs (Chemistry)

Personnel: P. D. Fleming (Chemistry), C. Cohen (Chemistry), J. Gordon (Chemistry) and Arthur Yang (Chemistry)

Publications: Cohen, C., and Fleming, III, P. D., "Solid Hydrodynamics," Phys. Rev. B., (in press).

Cohen, C., Fleming, III, P. D., and Gibbs, J. H., "Hydrodynamics and Light Scattering of Amorphous Solids," Phys. Rev. B, (to be submitted).

Supported by the National Science Foundation.

X-ray Photoemission Studies of Amorphous and Crystalline As_2S_3 and As_2Se_3.

As_2S_3 and As_2Se_3 are members of an important group of amorphous semiconductors that are quenchable from the melt and have useful optical transmission properties. A photoemission study was undertaken to determine the s and p character of their valence bands and the degree of bonding or non-bonding involved in the levels at the top of the valence band which affect the optical properties.

The valence band density of states in all four materials is generally similar, reflecting the similarity in atomic species and local coordination between the amorphous and crystalline forms. The upper region of the valence bands is separated from the lower portion by a minimum at about -7 eV relative to the top of the valence band, while the total widths are about 17 eV in all cases. The upper region of the valence band is generally double-peaked, most consistent with a model in which the uppermost level of the valence band is largely non-bonding. The separability of the valence band into two regions and the different photon energy dependence of electron emission from the lower relative to the upper region when using ultraviolet and X-ray phtoemission indicate that the lower region is s-like in character, the upper levels are largely p-like (bonding and non-bonding), and that the s-p hybridization is quite weak. These results contradict Hükel-type molecular orbital calculations which predict a 5 eV wide valence band with nearly complete s-p hybridization and support the use of more atomic-like basis sets for calculating the electronic structure of these inorganic glasses.

This work is part of a study of the relationship between the electronic structure of inorganic glasses and important properties of their bonding.

Principal Investigator: G. B. Fisher (Engineering)

Publications: Fisher, G. B., "X-ray Photemission Studies of Amorphous and Crystalline As_2S_3 and As_2Se_3," Bull. Am. Phys. Soc. 18, 1589 (1973).

Supported by the United States Army Research Office, Durham.

INTRODUCTION

Chemisorption on Metallic Surfaces

Investigations of solid surface phenomena have been carried out for a number of years at Brown University. In the past the research has involved separate programs in different departments, but efforts in this field are now being co-ordinated and given a common focus, namely studies of chemisorption on solid surfaces. The complexity of the chemisorption process indicates that an interdisciplinary approach to the problem should be fruitful.

The studies outlined in this report are limited to metallic systems. It is for these systems that progress in experimental and theoretical methods has been most rapid and they therefore provide the best opportunity for a direct interaction between experimentalist and theorists.

Most of the experimental work concerns the nature of chemisorbed species on well defined transition metal surfaces. The investigations include optical studies by Stiles, and LEED and AES studies by Estrup. Complementary work on transition metal compounds has been initiated by Risen. Ying has done theoretical calculations concerning the bonding of chemisorbed alkali and hydrogen atoms to metal surfaces and Quinn has used a related approach to investigate the properties of the electron density profile at the surface.

Together these studies represent the beginning of a concerted effort to formulate detailed models on which a description of the surface interactions may be based.

SECTION 4

Individual Contributions

Chemisorption on Metallic Surfaces

Optical Spectroscopy of Surfaces

We have continued to develop the new spectroscopic technique which we described in the report of the previous year. This technique involves the precise measurement of adsorbate-induced changes in the optical reflectance as a function of photon energy on clean metal surfaces. The understanding of the results of these studies has advanced significantly in the last year. Of particular importance is a detailed study which we have carried out with gases of H_2, CO, and O_2 on a clean W(100) surface. Investigations were carried out in photon energy range between .6 eV and 4.8 eV for coverages up to one monolayer. Detailed information on surface state binding energies was obtained from a study of the position of prominent peaks and dips in the $\Delta\epsilon_2$ structure. Investigation of the W(110) surface was undertaken. Preliminary results display the difference between the two surfaces which has been observed by other techniques of study in clean metal surfaces. Further investigation of the Mo(100) surface was also carried out.

Principal Investigator: P. J. Stiles (Physics)

Personnel: G. W. Rubloff (Physics) and M. A. Passler (Physics)

Publications: Anderson, J., Rubloff, G. W., Passler, M. A., and Stiles, P. J., "Surface Reflectance Spectroscopy (SRS) Studies of Chemisorption on W(100)," J. Vac. Sci. Technol., Vol. 11, No. 1, (1974).

Anderson, J., Rubloff, G. W., Passler, M. A., and Stiles, P. J., "Optical Reflectance Spectroscopy of Surface States in H_2 Chemisorption on W(100)," Physical Review Letters, Vol. 32, No. 12 (1974).

Anderson, J., Rubloff, G. W., Passler, M. A., and Stiles, P. J., "Surface Reflectance Spectroscopy Studies of Chemisorption on W(100)," Physical Review B, Vol. 10, No. 6 (1974).

Supported by the United States Army Research Office (Durham).

Dynamic Response Function of a Metal Surface

The density functional is applied to the problem of how a metal surface responds to an electromagnetic disturbance of arbitrary space and time dependence. The resulting hydrodynamic equations have been investigated for the case of self-sustaining oscillations. In addition to the regular surface plasmon, we find that additional surface modes can occur for sufficiently diffuse surfaces. The frequency and dispersion of these modes and their dependence on the electron density profile at the surface have been studied.

Principal Investigator: J. J. Quinn (Physics) (in collaboration with S. C. Ying)

Personnel: A. Eguiluz (Physics)

Publications: Eguiluz, A., Ying, S. C. and Quinn, J. J., "Influence of the Electron Density Profile on Surface Plasmons in a Hydrodynamic Model," Phys. Rev. B 15 (1975)

Supported by the National Science Foundation.

Adsorption and Surface Reactions

LEED and AES Studies

The chemisorption of several gases on the molybdenum (100) surface was studied using a combination of techniques, including LEED, Auger electron spectroscopy (AES), work function measurements and flash desorption. The investigation of hydrogen adsorption was emphasized in order to obtain data for comparison with W(100) + H_2 which has been studied extensively in this and other laboratories. A series of new hydrogen overlayer structures were found on Mo(100) and the two-dimensional "phase-diagram" (coverage vs. temperature) was established. The phase transformations include the "precipitation" of an ordered (4x2) structure from a lattice gas, and a

reversible order-disorder transformation from the (4x2) to a c(2x2) structure. The results suggest that the effective interaction between a pair of adsorbed H atoms on adjacent sites is repulsive at low T but attractive at room temperature.

Other experiments have been started to explore the interaction of O_2, CO, and CO_2 with the Mo(100) surface. Among the preliminary results is the finding that the AES oxygen signal is much smaller than predicted for the c(2x2) structure formed by CO adsorption. This result implies that either CO dissociates on this surface, or that the AES signal depends strongly on the bonding at the surface. The CO_2 data suggest that the latter possiblity should be ruled out.

Principal Investigator: P. J. Estrup (Physics and Chemistry)

Personnel: C. H. Huang (Chemistry), T. E. Felter (Phyics) G. B. Fisher (Engineering)

Publications: Huang, C. H., and Estrup, P. J., "Hydrogen Adsorption on Mo(100) at Low Temperature," Bull. Am. Phys. Soc. 19, 357 (1974) Separate paper to appear.

Taylor, T. N. and Estrup, P. J., "The Interaction of Hydrogen with Ni(110), "J. Vac. Sci. Techn. 11, 244 (1974).

Fisher, G. B. and Estrup, P. J., "Extreme Broadening of the 4p Levels in Fifth Period Elements," Bull. Am. Phys. Soc. 19, 233 (1974). Separate paper to appear.

Supported by the National Science Foundation.

Chemisorption on Metallic Surfaces

The density functional theory was applied to the problem of alkali metal atoms adsorbed on metallic surfaces. A series of alkali metals were studied. Heats of desorption, work function changes and equilibrium positions of the adsorbed species were calculated. The theory produces the correct trends among the alkalis and theoretical values for various physical quantities are in good agreement with experimental results.

Principal Investigator: S. C. Ying (Physics)

Personnel: L. M. Kahn (Physics)

Publications: Bendow, B. and Ying, S. C., "Phonon-induced Desportion of Adatoms from Crystal Surfaces--I Formal Theory," Phys. Rev. B7, 622 (1973).

Bendow, B., and Ying, S. C., "Phonon-induced Desorption of Adatoms from Crystal Surfaces--II Numerical Computations for a Model System," Phys. Rev. B7, 637 (1973).

Smith, J. and Kohn, W., and Ying, S. C., "Charge Density and Binding Energy in Hydrogen Chemisorption," Phys. Rev. Letters 30, 610 (1973).

Ying, S. C., "Hydrodynamic Response of Inhomogeneous Metallic Systems," Il Nuovo Cimento, Vol. 23 B, N.1, 270-281 (1974).

Smith, J., Kohn W., and Ying, S. C., "Chemisorbed Hydrogen: Electron Scattering Resonance Level and Vibrational Frequency," Solid State Commun., in press.

Supported by the Alfred P. Sloan Foundation Fellowship, the National Science Foundation and the Advanced Research Projects Agency.

Resonance Raman Studies of Chemisorption Model Complexes

The Raman spectra of ligand-metal complexes which have metal to ligand charge transfer absorptions in the region of the source frequency are studies as models for investigating chemisorption species. The series $[Fe(bipyridyl)_{3-x}(CN_{2x}]^{(-2x+2)}$ $(x = 0,1,2)$ was studied, and it was found that the vibrations of the complexed bipyridyl ligands are reasonantly enhanced as the Raman source is varied through the visible region containing the metal-ligand charge transfer band. Further, specific legand modes are selectively enhanced, and through analysis of the frequency dependence of the enhancement it was determined that the inclusion of the excited state vibrational frequency is important and leads to correlation of the identity of the resonantly enhanced bands with the nature of the absorption bands and the bonding in the charge-transferred excited states of the complexions.

Principal Investigator: W. M. Risen, Jr., (Chemistry)

Personnel: V. K. Mitra (Chemistry) and P. J. Miller (Chemistry)

Publications: Mitra, V. K., Miller, P. J., and Risen, Jr., W. M., "Resonance Raman Study of Complexes with Metal-ligand Charge Transfer Absorption," submitted, J. Chem. Phys.

Supported by the National Science Foundation.

Summaries of Other Related Work

Theoretical Study of Electron-Electron Interactions in a Two-Dimensional Electron Gas - J. J. Quinn (Physics) - See Section 7.

INTRODUCTION

Chalcogenide Materials

Several binary metal chalcogenides are being used commercially in the field of catalysis (CoS_2,MoS_2) as desulfurizing catalysts and for the manufacture of photovoltaic energy conversion cells (Cu_2S/Cds), and new platinum metal chalcogenides are being prepared and characterized at this laboratory. These compounds may have potential use in the field of catalysis.

The Cu_2S/CdS cell is being considered as a viable, cheaper option to silicon for photovoltaic energy conversion. However, the complex chemistry of the Cu_2S/CdS system and the resulting cell instability requires a further detailed study of these materials. This has lead to coordinated efforts by Professors Loferski, Tauc, Glicksman and Wold to study both the Cu_2S system as well as to find other direct band gap semiconductors which may be potential candidates for energy conversion.

SECTION 5

Individual Contributions

Chalcogenide Materials

Transition Metal Chemistry

I. Crystal Growth and Characterization of $Pt_{0.97}S_2$

Large, well-formed plates of $Pt_{0.97}S_2$ were grown by chemical vapor transport. A combination of phosphorus and chlorine was used as the transport agent. The best crystals were grown when the charge zone was maintained at 800°C and the growth zone at 740°C. The crystals were found to be diamagnetic with a susceptibility of -31(2) x 10^{-6} emu/mole at 77°K and showed semiconducting behavior with a band gap of 0.20(2)eV. From Hall voltage measurements, the sign of the carriers was ascertained to be positive. $Pt_{0.97}S_2$ particles less then 63μ underwent thermal decomposition in air at 270(10)°C.

II. Crystal Growth and Characterization of PtP_2

Large, well-formed crystals of platinum diphosphide, PtP_2, were grown from a tin flux. These crystals were shown to be of good quality by magnetic, density, and crystalloraphic measurements. However, the presence of tin (0.02%) as an impurity prevented meaningful measurements of the electrical properties of PtP_2. The crystals were found to be diamagnetic, with a susceptibility of -64 x 10^{-6} emu/mole. The positions of the phosphorus atoms within the crystal structure were re-determined by measuring the intensities of 32 x-ray reflections. The P-P bond distance was then calculated to be 2.22(2)Å.

III. Preparation and Characterization of Compounds of the System $FeAs_{2-x}Se_x$

Compounds of the system $FeAs_{2-x}Se_x$ were synthesized both as polycrystalline powders by direct combination of the elements and as single crystals by chemical vapor transport. Electrical and magnetic measurements were made on well-characterized samples. These measurements showed that the substitution of selenium for arsenic in the diamagnetic semiconductor $FeAs_2$ results in metallic, paramagnetic behavior. These results are consistent with a band model proposed by Goodenough for compounds crystallizing in the marcasite structure.

IV. Preparation and Properties of the System CoP_xS_{2-x}

Lattice parameters were determined for members of the system CoP_xS_{2-x} ($0 \leq x \leq 1$). A cubic region was observed for $0 \leq x \leq 0.5$ and a tetragonal region for $0.5 < x \leq 1$. Magnetization and susceptibility measurements were made on the sample CoP_xS_{2-x} ($0 \leq x \leq 0.5$) from 4.2 to 500°K and to 9.5k0e. The ferromagnetic Curie temperature decreased almost linearly with composition from a value of 122(1)°K for x=0 to 23(1)°K at x-0.3. The saturation magnetization passed through a maximum at 41.5(2) e.m.u./g at x=0.05, increasing from 40.0(2) e.m.u./g for x-0, and then decreased to below 15 e.m.u./g for x-0.3. The paramagnetic data gave a P_{eff}^2/Co^{2+} that increased linearly with phosphorus substitution from 4.4(2) μ_B^2 at x=0.5. The Weiss constant decreased almost linearly from 150(3)°K for x=0 to 85(2)°K for x=0.3. The magnetic properties of this system are compared with those of the system $CoAs_xS_{2-x}$. Changes, with composition, in the Curie and Weiss temperatures are almost identical in the three systems for $x \leq 0.25$. As with $CoAs_xS_{2-x}$ the ferromagnetic moment reaches a maximum at 2=0.05 and then decreases with increasing x, although the magnetic interactions remain ferromagnetic for all $x \leq 0.5$.

V. Preparation and Characterization of Some CoXY Compounds Where Y=P, As, Sb and Y=S, Se[1].

The lattice parameters for the CoXY series of compounds where X=P, As, Sb and Y-S, Se were determined. CoPS is tetragonal, CoAsS is cubic, CoSbS and CoPSe are orthorhombic, and CoAsSe and CoSbSe are "anomalous" marcasites. Partial ordering of As-S pairs was found for ground single crystals of CoAsS. Magnetic measurements made on the CoXY type compounds showed weak, temperature-independent paramagnetism except for CoSbS, which was diamagnetic. Electrical data indicate that the specific anion appears to affect the nature of the electrical properties.

VI. Preparation and Characterization of the Solid Solution Series $Co_{1-x}Ni_xAsS$ ($0 \leq x \leq 1$)

Both single crystal and polycrystalline samples of the series $Co_{1-x}Ni_xAsS$ $0 \leq x \leq 1$ have been prepared. The materials have been characterized by x-ray diffraction, density and chemical analysis. X-ray intensity data collected for the end member NiAsS shows anion ordering consistent with the ullmanite structure (space group $P2_13$). Magnetic data indicate that nickel (d^7) is present in the low-spin state. Electrical data show that one additional electron/Ni atom is contributed to the otherwise empty σ^* band of CoAsS.

VII. Preparation and Characterization of the System $CuGa_{1-x}Fe_xS2$

Polycrystalline samples of the solid solution series $CuGa_{1-x}Fe_xS_2$ ($0 \leq x \leq 1.0$) have been prepared by direct combination of the elements. X-ray diffraction analysis and density measurements have indicated that all members of the $CuGa_{1-x}$- Fe_xS_2 system ($0 \leq x \leq 1.0$) crystallize with the chalcopyrite structure. Magnetic susceptibility data have shown that when x=0.025, the observed moment for the iron approaches the spin-only values of $5.92\mu_B$ caluculated for high-spin iron (d^5). Deviations from the spin-only moment become appreciable when $x \geq 0.1$. Mossbauer spectra show at temperatures above 77°K the onset of antiferromagnetic order when $x \geq 0.5$.

VIII. Preparation and Properties of Iron Phosphorus Triselenide, $FePSe_3$ [1a]

Iron phosphorus triselenide, $FePSe_3$, has been prepared by chemical vapor transport using 75 Torr of chlorine gas as a transport agent and a temperature gradient of 650→610°C. The structure of $FePSe_3$ (space group R3) is related to that of CdI_2. Selenium atoms are in a hexagonal, close-packed array with iron atoms and phosphorus-phosphurus pairs (2:1 ratio) occupying the trigonally distorted octahedral holes in an ordered arrangement. Magnetic susceptibility measurements show that the compound orders antiferromagnetically at 123 (2)°K; Mossbauer effect measurements indicate the principal axis of magnetization is along the crystallographic (hexagonal) c axis. The paramagnetic moment and Mossbauer data obtained above the ordering temperature indicate that the iron ions exist in the divalent high-spin state.

IX. Optical Band Gap Variation in the System $(GaP)_{1-x}(ZnSe)_x$ for $0 \leq x \leq 0.18$

Measurements of the optical absorption of single crystalline samples of $(GaP)_{1-x}$ $(ZnSe)_x$ show a sharp drop in the indirect band gap as x is increased from 0 to 0.02, followed by a gradual increase as x is increased to 0.18. The maximum decrease observed is ~0.16 eV at room temperature. It is suggested that the band gap is narrowed in the solid solutions as a result of the high density of ions in these non-isoelectronic mixed systems.

X. Extended Interactions in Transition Metal Oxides and Chalcogenides - ACS Symposium Series #5

Principal Investigator: A. Wold (Chemistry and Engineering)

Personnel: R. J. Arnott (Engineering), R. Beaulieu, (Engineering), P. Russo (Engineering), R. Kershaw (Engineering), A. Baghdadi (Chemistry), H. Nahigian (Chemistry), J. Steger (Chemistry), H. McKinzie (Chemistry), M. DiGuiseppe (Chemistry), B. Taylor (Chemistry), A. Catalono (Chemistry), D. Schleich (Chemistry), J. Ackerman (Chemistry), S. Soled (Chemistry), A. Finley (Chemistry.

Publications: Baghdadi, A. and Wold, A., "Preparation and Characterization of Compounds of the System $FeAs_{2-x}Se_x$," J. Phys. Chem. Solids, 1974, Vol 35, pp. 811-815.

Nahigian, H., Steger, J., Arnott, R. J., and Wold, A., "Preparation and Properties of the System CoP_xS_{2-x}," J. Phys. Chem Solids, 1974, Vol. 35, pp 1349-1354.

Nahigian, H., Steger, J., McKinzie, H. L., Arnott, R. J., and Wold, A., "Preparation and Characterization of Some CoXY Compounds Where X=P, As, Sb and Y=S,Se[1]," Inorganic Chemistry, 13, 1498 (1974)

Steger, J. J., Nahigian, H., Arnott, R. J., and Wold, A., "Preparation and Characterization of the Solid Solution Series $Co_{1-x}Ni_xAsS$ $(0 \leq x \leq 1)$," J. of Solid State Chemistry, 11, 53-59 (1974).

DiGiuseppe, M., Steger, J., Wold, A., and Kostiner, E., "Preparation and Characterization of the System $CuGa_{1-x}Fe_xS_2$," Inorganic Chemistry, 13, 1828 (1974).

Taylor, B., Steger, J., Wold, A., and Kostiner, E., "Preparation and Properties of Iron Phosphorus Triselenide, $FePS_3$[1a]," Inorganic Chemistry, 13, 2719 (1974)

Catalano, A., Beaulieu, R., Gregg, T., Head, P., Wold, A., Glicksman, M., "Optical Band Gap Variation in the System $(GaP)_{1-x}(ZnSe)_x$ for $0 \leq x \leq 0.18$," Solid State Communications Vol. 14, pp. 421-425, 1974.

Supported by the National Science Foundation and the United States Army.

Lattice Dynamics of Tetrahedrally Bonded Semiconductors Containing Ordered Vacant Sites

M_2X_3 compounds (where M = Al, Ga or In; and X = S, Se or Te) are characterized by a crystal structure based on a tetrahedral atomic coordination as in the zinc-blende structure. However, one third of the cation sites available to A atoms are vacant. These compounds represent an interesting case of solids with completely satisfied chemical bonds but with a very large concentration of vacancies. Furthermore, the vacancies may exist in an ordered or disordered state in the same material (e.g., in the α and β phases of In_2Te_3, respectively).

Infrared and Raman spectra of defect structure semiconductors In_2Te_3, Ga_2Se_3 and Ga_2S_3 with ordered vacant sites were measured on polycrystalline samples and analyzed. The interpretation of the observed spectra is based on the existence of uninterrupted chains of tetrahedra along the directions interconnecting the two next nearest neighbors (the [110] direction in the cubic lattice). Arguments are presented to show that the phonons propagating along this direction dominate the spectra, and that in the first approximation their frequencies can be obtained by a six-fold folding of the Brillouin zone of the simple zinc-blende structure in the [110] direction. The observed spectra were fitted by a rigid-ion model of the corresponding zinc-blende structure, and the dispersion relations for this structure were obtained. It is shown that the defects affect the central forces between the nearest neighbors only slightly while the non-central forces are changed more significantly. The softening of a mode in In_2Te_3 may point out an instability of its ordered structure.

The more extensive experimental data and their analysis summarized above confirmed our original interpretation of the vibrational spectra of semiconductors with a defect zinc-blende structure (Finkman and Tauc, Phys. Rev. Lett. 31, 890 (1973).

Principal Investigators: J. Tauc (Engineering and Physics)
A. Wold (Chemistry and Engineering)

Personnel: E. Finkman (Engineering) and R. Kershaw (Engineering)

Publications: Finkman, E., Tauc, J., Kershaw, R., and Wold, A., "Lattice Dynamics of Tetrahedrally-Bonded Semiconductors Containing Ordered Vacant Sites," Phys. Rev. B15, May 15 (in print),

Supported by the National Science Foundation.

Optical Properties, Band Structure and Lattice Vibrations in the $(CuInSe_2)_{1-x}$ - $(2ZnSe)_x$ System

This work is aimed at the elucidation of the relationship of the electronic properties and lattice vibrations in ternary and isolelectronic binary compounds. The experimental methods include studies of the absorption edge, reflection spectroscopy in a broad frequency range (from the far infra-red into the vacuum UV region), infrared and Raman spectroscopy. The main problems are the understanding of the influence of the structural change from the sphalerite to the chalcopyrite structure, of the disorder and of the d-bands of Cu atoms.

The work was done on single crystals which had the chalcopyrite structure for $x \leq 0.43$ and the sphalerite structure for $x \geq 0.48$. At the absorption edge the absorption constant was found to be proportional to $(h\omega-Eg)^{1/2}$, indicating direct transitions in the whole composition range. The absorption edge $E_g = 1.02 - 0.24x + 1.8x^2$ (eV) without any discontinuity at the phase transition.

A band near 3 eV was observed for all compositions in the chalcopyrite structure but was not seen in the sphalerite phase. Its abrupt disappearance from $x = 0.43$ to $x = 0.48$ indicates that it may not be due to transitions from the copper d-levels to the lowest conduction band but may be associated with interband pseudo-direct transitions which become allowed by zone folding.

Experimental work on the UV reflection spectra, infra-red and Raman spectra has been completed and is being analyzed and interpreted.

Principal Investigator: J. Tauc (Engineering and Phyics)

Personnel: J. N. Gan (Physics)

Publications: Gan, J. N., Tauc, J., Lambrecht, Jr., V. G. Robbins, M., "Optical Properties of the $(CuInSe_2)_{1-x}$ $(2ZnSe)_x$ System. Bull. APS 19, 308 (1974).

Gan, J. N., Tauc, J., Lambrecht, Jr., V. G.,Robbins, M., "On the 3d Electron Contribution to the Electronic Structure of Ternary I-III-VI_2 Compounds," Solid State Communications 15, 605 (1974).

Supported by the United States Army and the National Science Foundation.

Investigation of Thin Film Solar Cells Based on Cu_2S and Ternary Compounds of the Type $CuInS_2$ and $CuInSe_2$ for Large Scale Terrestrial Solar Energy Utilization

The program has as its goal the development of thin film solar cells based on Cu_2S and $CuInS_2$. Our object has been to produce thin layers of these semiconductors (which have favorable characteristics for use in solar cells) by "sulfurizing" thin (≥ 1000Å) layers of Cu and CuIn alloy on various substrates. Sulfurization is accomplised by heating the metal film to temperatures of several hundred degrees centigrade in a flowing mixture of $H_2S + H_2 + Ar$. The substrates used include silica slides, pyrex, Si single crystals and CdS single crystals. We have found that it is now possible to select a combination of reaction temperature and gas composition which results in a film consisting of Cu_2S only. Those films which contain Cu_2S can be identified because they exhibit the luminescence spectrum of Cu_2S. We have fabricated cells consisting of p-Cu_xS on n-Si; they have an estimated solar energy conversion efficiency of a few tenths of a percent ("goog" solar cells would have an efficiency in excess of about 5%). The work on $CuInS_2$ has been mainly concerned with attempting to grow single crystals of this semiconductor because it should be easier to evaluate the potential of this materials as a solar energy converter by making cells from single crystals. Cathodoluminescence studies of this material show that the spectrum emitted by $CuInS_2$ depends on the extent to which the sulfur content deviates from stoichiometry.

Principal Investigators: J. J. Loferski (Engineering) and A. Wold (Engineering and Chemistry)

Personnel: J. Shewchun of McMaster University, Hamilton, Ontario, Canada; R. J. Arnott (Engineering); S. Mittleman, (Engineering); G. Adeboyega (Engineering); H. Hwang, (Engineering); A. Loshkajian (Engineering); J. Wu, (Engineering); E. Crisman, (Engineering) R. Beaulieu,(Engineering); and P. Maciel, (Engineering).

Publications: First and Second Semiannual Reports NSF/Rann Grant GI-38102X "Investigations of Thin Solar Cells, etc." issued in January 1974 and July 1974. Edited by J. J. Loferski.

Mittleman, S., Brown University Technical Report "Cathodoluminescence Studies of the Cu-S system and of $CuInS_2$," Phd. Thesis granted in June 1974.

Presentations at NSF Solar Energy Workshops May 1974 (University of Arizona), June 1974, Pasadena, California

Supported by the National Science Foundation and the Rann Solar Energy Conversion Program.

Investigation of the Properties of New Semiconducting Alloys and their Application to Luminescent Devices

Continuing success in the growth of large, high quality single crystals of solid solutions of GaP and ZnSe yielded excellent data on the optical absorption, but did not yield material of high conductivity. Attempts to introduce doping impurities were not successful.

The optical absorption data covered the range of absorption coefficient from 10 cm^{-1} to over 10^4 cm^{-1}. Crystals with less than about 8% ZnSe showed the same dependence on energy of the optical absorption coefficient, and verified the previously suggested sharp decrease in band gap. For crystals between 8 and 18%, tne optical absorption has a different dependence on energy, showing a more rapid variation at the lower energies. The energy gap is observed to shrink by about 0.16 eV, for additions of ZnSe of only 3% or less; it then increases gently with further additions of ZnSe.

It is suggested that the rapid decrease (observed for all solid solutions in which the crystals are diamond-like in bonding, but the substitutional pairs are not iso-electronic) seen here and in other similar solid solutions is the result of the large contribution to the Hamiltonian from the Coulombic potentials of the atoms having "charge" in the crystal, i.e., the Zn and Se atoms will be much like an acceptor and donor in the case where they are dilute in concentration.

Principal Investigators: M. Glicksman (Engineering) and A. Wold (Engineering and Chemistry)

Personnel: A. Catalano (Engineering), R. Beaulieu (Engineering), S. A. Mittleman (Engineering), T. Gregg (Engineering), K. Burbank (Engineering), L. Mang (Engineering) and I. Mykyta (Physics).

Publications: Catalano, A., Beaulieu, R., Gregg, T., Head, P., Wold, A., and Glicksman, M.,"Optical Band Gap variation in the System $(GaP)_{1-x}(ZnSe)_x$ for $0 \leq x \leq 0.18$," Solid State Communications 14, 421-5.

Summaries of Other Related Work

X-Ray Photoemission Studies of Amorphous and Crystalline As_2S_3 and As_2Se_3 - G. B. Fisher (Engineering) - See Section 3

SECTION 6

Alloy Design and Synthesis of Microstructures for Specific Properties

Theoretical and Experimental Studies of Thermodynamic, Fluid Dynamic and Metallurgical Phenomena in Electric Discharge Machining

The primary objective of this study is to present more information about the spark-machining process. Particular attention was given to:

(i) detailing the integrated view of the complete process;

(ii) setting up an appropriate energy transfer model of the anode, and then finding the local temperature history of the solid as well as predicting the heat-affected zones of steel;

(iii) setting up an appropriate model to study the main mechanism of metal removal;

(iv) coupling the analyses of (ii) and (iii), the estimation of the erosion rate by a single spark being then formulated;

(v) careful study of the spark-machined surface and establishment of the probable mechanisms of metal bubble formation;

(vi) metallurgical study of the heat-affected zones for understanding the spark-machining effects on the properties of steel.

Principal Investigators: P. D. Richardson (Engineering)
J. Gurland (Engineering)

Personnel: C. H. Chen (Engineering)

Publications: Ph.D. Thesis, July 1974, C. H. Chen

Suppored by the Avanced Research Projects Agency.

A Study of the Indentation Hardness of Cemented Tungsten Carbide

(i) The relation of the Vickers indentation hardness of cemented tungsten carbide to its microstructural parameters can be represented by the Hall-Petch type equation. The value of Hall-Petch constant H_{oy} and K_H are given as 440 kg/mm^2 and 15.2 kg/mm^2, respectively. The nominal mean free path of cobalt layers is proposed as the strength controlling microstructural parameter.

(ii) The contiguity which was reported to be an important microstructural parameter in TaC-Co alloys gives only a small contribution to the strength of cemented tungsten carbide alloys.

(iii) The hardness values of alloys with small mean free path are low in comparison to the expected values of the Hall-Petch relation. This is thought to be a result of the failure of the binder phase during indentation or a result of the plastic deformation of the carbide particles at stress concentrating points such as triple boundary intersections.

(iv) From the results of the present work, it might be deduced that, during the hardness indentation, the pastic deformation is mostly concentrated in cobalt layers while the carbide deforms mainly elasticially.

Principal Investigator: J. Gurland (Engineering)

Personnel: Hu-Chul Lee (Engineering)

Publications: Masters Thesis, June 1974, H. C. Lee

Supported by the Advanced Research Projects Agency.

Thermomechanical Processing of β Titanium

Work has continued on Thermo mechanical processing of β Titanium. Five additional heats of varying chemistry have been produced and are being investigated to optimize the mechanical properties. Continued work on mechanical properties has yielded the following results:

(i) Improved unaged tensile strengths, 240,000 psi with 50-60% RA.

(ii) Notch strength ratio is greater than 1.5 up to 250,000 psi yield strength.

(iii) Fatigue limit for wire heat treated to 332,000 psi is between 140,000 and 150,000 psi.

(iv) Stress Corrosion susceptability is > 185,000 psi, 56% of UTS, for H_2O-3% NaCl and > 150,000 psi, 45% of UST for CH_3OH -1% HCl.

Electron microscopy has finally begun to yield reasonable thin foils. The structure at low deformations shows planar arrays of long straight dislocations quite atypical of b.c.c. materials. At large deformations cells do form, however, they never coalese into clean boundaries but remain difuse with dense intercellular tangles.

Principal Investigator: D. H. Avery (Engineering)

Personnel: N. W. Polan (Engineering) and E. Savage (Engineering)

Publications: Avery, D. H., and Polan, N. W., "An Optimal Design of a High Strength, Ductile Metallic Material: Criteria and Application to a β-Titanium Alloy", Met. Trans. vol. 5, 1974, p. 1159.

Avery, D. H., Polan, N. and Ball, A., "On the Strength of a β Phase Titanium Alloy," Proc. of Elec. Mic. Soc. of Southern Africa, vol. 4, p. 85.

Polan, N. W. and Avery, D. H., "Mechanical-Thermal Processing of a β-Titanium Alloy," submitted to Met. Trans.

Polan, N. W., "Microstructural Strengthening Criteria and Application to a β Titanium Alloy," Brown Ph.D. Tbesis, available as Brown Report.

Supported by the Advanced Research Projects Agency and The University of Cape Town, Republic of South Africa.

Effect of Processing Parameters on the Reaction Sintering of Silicon Nitride

Detailed microstructural examination of reaction bonded silicon nitride and its relation to processing conditions and mechanical properties has continued during this investigating period. Scanning electron, transmission electron, and optical microscopes as well as X-Rays have been used to characterize the microstructure of 1 inch diameter by .4 inch thick discs. These discs have been produced in a nitrogen atmosphere at temperatures up to an including 1550°C. Many kinds of temperature vs time cycles have been studied but a typical run consists of 24 hours at 1350°C followed by 5 hours at 1450°C. Other variables considered are gas flow rate, rate of heating, average Si particle size, various contaminents in the gas such as H_2O and O_2, and impurities in powder, particularly Fe.

Close examination of the literature indicates a large variation in final degree of reaction, α/β ratio and transverse rupture strength from one investigator to another. When all of the reported conditions are reproduced in our laboratory further discrepancies become apparent. In an effort to try and understand these differences a large number of experiments have been performed to establish a cause-effect relationship between processing parameters and final microstructure and bulk properties. Using these experiments, a working reaction mechanism can be constructed. It is becoming apparent that some important variables are not recognized and are not consistanly reported in the literature. Handling and pressing techniques for the powder, heating rate and details of gas flow through furnace are amongst the variables which can produce large variations and are not always reported.

These and other variables are important because they change the morphology of the reacted Si_3N_4. The microstructure consists of needles, matte, spikes, blades, unreacted and reacted grains and pores, and each contributes to the bulk density and transverse rupture strength in different ways. All of the microconstitutents are divided between the α and β form of Si_3N_4 and different reaction mechanisms apply in each case, making the system complex.

This investigation has lead to the establishment of many cause-effect relationships and a working model of reaction mechanisms. Such things as degree of porosity, α/β ratio, final density (without varying green density) and variation of certain microconstituents can be controlled. Gaining this control has been very encouraging and should lead to the ability to design for specific engineering applications.

Principal Investigator: M. H. Richman (Engineering)

Personnel: H. M. Jennings (Engineering), S. C. Danforth (Engineering) and J. Fogarty (Engineering)

Publications: None

Supported by the United States Army Research Office, Durham.

Titanium Carbide Coated Cemented Carbide Cutting Tools

Chemical vapor deposition of a coating of TiC on a cemented carbide tool produces an intermediate layer approximately one micron thick of Co_6W_6C (eta carbide) between the substrate and the three micron thick TiC layer. Although the TiC coated cemented carbides have a tool life lasting up to four times longer than the uncoated tools, the effect of the intermediate eta phase on this tool life has not been known to date. This research has been investigating the effect of the eta carbide layer on tool life by preparing TiC sputter-coated tools both with and without the eta layer. The eta carbide target material for the sputtering system was prepared by powder metallurgy techniques in a hydrogen furnace. The sputter-coated eta layer goes on the substrate in an amorphous manner at all times and must be heat treated to make it crystalline. The TiC sputter-coated layer goes on either amorphously or in a crystalline manner depending upon the substrate temperature and surface. If the substrate is cooled to room temperature during coating or if the substrate has already been coated with the eta carbide, the TiC sputter coating goes on amorphously; but if the substrate is not cooled during coating and if the TiC coating goes directly onto the cemented carbide, the TiC coating is crystalline. Adhesion between the sputtered coatings and the substrate is poor, and heat treating must be employed to bond the coating well to the substrate.

Tool life tests with the sputter coated tools show that the eta layer does improve tool life in uninterrupted cutting. A 0.5 micron layer of the eta carbide increased tool life by 50%, and 0.25 micron layer on TiC only increased tool life by 100%. These results show that the eta coating does indeed improve tool life, but that the TiC coating is more effective. Thus this indicates that the eta carbide layer in the combined TiC/eta coatings may be partially responsible for the extended tool life observed in the commercially coated tools which have coatings comprised of both TiC and eta carbide.

Principal Investigator: M. H. Richman (Engineering)

Personnel: W. D. Sproul (Engineering) and J. W. Fogarty (Engineering).

Publications: Sproul, W. D., and Richman, M. H., "Effect of the Eta Layer on TiC Coated Cemented Carbide Tool Life," to appear in Science and Technology in July-August 1975. Paper was presented at the Second Conference on Structure-Property Relationships in Thick Film and Bulk Coatings in San Francisco, California on February 11, 1975.

Lee, M. and Richman, M. H., "Some Properties of TiC Coated Cemented Carbides," to appear in Metals Technology, November 1974.

Supported by the Advanced Research Projects Agency.

Fabrication of Ternary Alloy Light Emitting Diodes for Methane Gas Detection

Work has continued on the development of infrared light emitting diodes near the composition $In_{0.95}Ga_{.05}As$ having a room temperature emission band centered at 3.31 microns, the methane absorption band. Efficient junction InAs detectors were also fabricated, using Cd diffusion into n-type material.

Work has concentrated on reproducibility of the device characteristics by controlling the various stages in the production of the devices. The optical system is being optimised with respect to pathlength, light collecting efficiency and dimensions.

Compensation methods of the effects of dust, water vapor and temperature change were developed. Since the bandgap of the diodes as well as their efficiency are temperature dependent, the signal strength (% CH_4) is temperature dependent and calculations and tests were performed to determine the optimal composition and best apparatus design for a near room temperature range.

Successful laboratory performance of an infrared methane detector was demonstrated. Several Central Facilities have been used in material testing.

Principal Investigator: H. J. Gerritsen (Physics)

Personnel: C. Taylor (Physics), E. Crisman (Engineering), and J. Beall (Physics)

Publications: Gerritsen, H. J., Patterson, W. R., and Mora, N. A., "Methane Detection Using a Light Emitting Diode," Proceedings of the First WVU Conference on Coal Mine Electrotechnology (1972).

Gerritsen, H. J., Taylor, C. C., Reumna, S. R., and Crisman, E. E., "A Methane Detection Unit Using a Light Emitting Diode," Proceedings of the Second WVU Conference on Coal Mine Electrotechnology (1974).

Supported by the United States Bureau of Mines.

Summaries of Other Related Work

A Combined Macroscopic and Microscopic Appraoch to the Fracture of Metals - J. Gurland (Engineering) and J.R. Rice (Engineering) - See Section 2

Problems in Strong Interaction Physics - A. Houghton (Physics) - See Section 8

SECTION 7

Plasmas in Solids

Two-Dimensional Plasmas

We have continued the rewarding studies of two-dimensional plasmas, either electron or hole plasmas. One striking feature of this physically obtainable experimental system is that one is able in a MOSFET structure to vary the density of the plasma, and therefore to look for the influence of many-body effects. We have continued this investigation and reported work in which observations on the hole plasmas were observed for the first time. Amplitude dependence indicates that the dominant variation in the energy-splitting of carriers in the single electric subband is a non-parabolic effect and not the many-body effect. Investigations were carried out for electron plasmas in additional crystalline surfaces, the (111) and the (110). Results were not what one would have expected and indicate microstrains in one case in the surface. The study of different surfaces appears to be leading to an understanding of the techniques for fabrication of the silicon silicon-dioxide interface which is valuable in itself as well as in device fabrication.

Principal Investigator: P. J. Stiles (Physics)

Personnel: A. A. Lakhani (Physics) and T. Theis (Physics)

Publications: Smith, J. L. and Stiles, P. J., "The Dependence of the Electron-Electron Enhancement of the Effective Mass on Magnetic Field," Low Temperature Physics-LT 13, Vol. 4, Plenum, New York.

Lakhani, A. A., Stiles, P. J., and Cheng, Y. C., "Oscillatory Magneto-conductance of p-Type Inversion Layers in Si Surfaces," Physical Review Letters, Vol. 32, No. 18 (1974).

Stiles, P. J., "Electronic Properties of Interface Carriers at Low Temperatures," Proceedings of the 2nd International Conference on Solid Surfaces (Kyoto 1973).

Supported by the National Science Foundation.

Theoretical Study of Electron-Electron Interactions in a Two-Dimensional Electron Gas

The magnetoplasma modes of a two dimensional electron gas in the presence of a dc magnetic field have been studied. For a free electron model cyclotron harmonic waves are found at frequencies close to $\omega = n\omega_c$ for $n = 2,3,4\ldots$. These modes are coupled to the plasmon which behaves as $\omega \alpha\ q^{1/2}$ for small wave number q. When Fermi liquid effects are included, the positions of the cyclotron harmonics are shifted due to Fermi liquid interactions. A microscopic theory of Fermi liquid interactions in the two dimensional electron gas is being developed.

Principal Investigator: J. J. Quinn (Physics)

Personnel: T. K. Lee (Physics)

Publications: Quinn, J. J. and Chiu, K. W., "Plasma Oscillations of a Two-Dimensional Electron Gas in a Strong Magnetic Field," Phys. Rev. B9, 4724 (1974).

Quinn, J. J. and Lee, T. K., "Fermi Liquid Theory of a Two-Dimensional Electron Gas: Magnetoplasma Modes," Phys. Rev. to appear.

Supported by the National Science Foundation.

Theoretical Studies of Condensed Electron-Hole Droplets in Semiconductors

At high density and low temperature, non-equilibrium carriers in semiconductors condense into "electron-hole droplets". The surface structure, surface energy and dipole barrier, and the temperature dependent surface tension of these droplets in Ge, Si and strained Ge has been obtained using a generalization of the Hokenberg-Kohn energy-density formalism. (P. Hokenberg and W. Kohn, Phys. Rev. B, 136, 864 (1964). The collective modes of these droplets, which consist of bulk and surface plasmons and low lying acoustic modes, have been obtained using an hydrodynamic approach, and the coupling of these modes to one another has been studied.

A non-interacting droplet model of the electron-hole liquid condensation has been developed and used to describe the liquid-gas-like phase diagram for this condensation. Using the above calculated surface tension, this model gives values of the critical density and temperature in reasonably good agreement with experiment. Fitting recent detailed

measurements of this phase diagram in Ge gives good agreement with experiment and provides an experimental estimate of the droplet surface tension. A Theoretical phase diagram has been constructed for Si for which detailed measurements have not yet been made.

Principal Investigators: S. C. Ying (Physics) and T. L. Reinecke (Physics)

Personnel: F. Crowne (Physics)

Publications: Reinecke, T. L., Crowne, F., and Ying, S. C., "Surface Properties and Collective Modes of Electron-Hole Droplets in Ge, Si, and Strained Ge," Proceedings of the XII International Conference on the Physics of Semiconductors, Stuttgart, 1974, ed. M. H. Pilkuhn.

Reinecke, T. L., and Ying, S. C., "Droplet Model of Electron-Hole Liquid Condensation in Semiconductors," Phys. Rev. Lett. (submitted for publication).

Supported by the National Science Foundation and A. P. Sloan Research Fellowship.

Studies of Plasmas in Semiconductors

Studies of the high density electron-hole plasmas at low temperatures continued, using germanium and both flash-lamp excitation and Nd:YAG laser excitation. Attempts to observe the (expected) charge on electron-hole drops, at about 1.8 K, were not conclusive. Initial observations which indicated a possible charge could not be repeated reproductibly, because of the noise pick-up which interfered with the observations.

Studies which now cover some 20 different crystals and with thicknesses varying from 35 microns to over 500 microns show that the previously-reported "plateau" in conductivity observed at low temperatures can be explained simply in terms of constant free carrier density over ranges of excitation varying by over a factor of 1000. Plateaus had values of conductivity which varied slowly with thickness: this fits well with a theory assuming that the conductivity depends linearly on the density and that the density is inhomogeneous through the thickenss because of recombination at the surface. The fit is good for a diffusion length of about 110 microns, which is a reasonable estimate for the observed lifetimes at 1.8 K.

Principal Investigator: M. Glicksman (Engineering)

Personnel: S. A. Mittleman (Engineering), Tat-Yin Choi (Engineering) and J. Meyer (Physics).

Publications: Glicksman, M., "Instablities in Semiconductor Plasmas," in Advances in Plasma Physics Vol. 5 (A. Simon and W. B. Thompson, ed.), pp. 261-279 (J. Wiley, 1974).

Glicksman, M., "Plasma Physics," 1973 McGraw Hill Yearbook of Science and Technology, pp. 345-347.

Supported by Brown University, through Project Overlord; and the National Science Foundation.

Summaries of Other Related Work

Chemisorption on Metallic Surfaces and e-H Condensation in Semiconductors - S. Ying (Physics) - See Section 4

SECTION 8

Low Temperature Properties of Materials

Problems in Strong Interaction Physics

In the past year we have been investigating several problems in strong interaction physics.

The renormalization group ideas developed by Wilson have been extended in several different directions.

(i) Exact renormalization group equations[1,2,3] have been used to discuss (a) corrections to scaling laws; (b) critical exponents of two and three dimensional systems.

(ii) Approximate renormalization group methods have been developed for discrete lattices in two and three dimensional systems.[4,5]

It is anticipated that extensions of these ideas along the lines used by Wilson in discussing the Kondo problem will be useful in discussing the properties of quasi-one dimensional systems. Previous methods, parquet algebra for example, clearly fail in the interesting case of an attractive particle-particle interaction. In work closely related to the above but extending into low temperature physics, we have been studying the effects of fluctuations (1-dimensional) on the transport properties of type II superconductors near their upper critical field H_{c2}. We have continued our investigation of the transport properties of the superfluid phases of He^3.[6] We are currently interested in the detailed effects of finite lifetime on spin transport in both 'A' and 'B' phases.

Principal Investigator: A. Houghton (Physics)

Personnel: O. T. Oriol (Physics) and M. C. Yalabik (Physics)

Publications: Wegner, F. J. and Houghton, A., "Renormalization Group Equation for Critical Phenomena,", Phys. Rev. A 8, 401 (1973). (1)

Wegner, F. J. and Houghton, A., "Feynman-Graph Calculation of the (0,1) Critical Exponents to Order ϵ^2," Phys. Rev. A, Vol. 10, No. 1, 435-437 (July 1974). (2)

Wegner, F. J. and Houghton, A., "Exact Renormalization Group Equations," Proceedings of the Temple Conference on Phase Transitions, 1973. (3)

Kadanoff, L. P. and Houghton, A., "Numerical Evaluations of the Critical Properties of the Two-Dimensional Ising Model," Proceedings of the Temple Conference on Phase Transitions, 1973. (4)

Kadanoff, L. P. and Houghton, A., "Numerical Evaluations of the Critical Properties of the Two-Dimensional Ising Model," Phys. Rev. B, Vol. 11, No. 1, 377-386 (January 1975). (5)

Valls, O. T. and Houghton, A., "On the Viscosity of Superfluid Helium^3, Phys. Lettrs., Vol. 50A, No. 3, 211-212 (December 1974); and to be published. (6)

Supported by the National Science Foundation.

Magnetic Properties of Rare Earth Ions in Metals

The resonance properties of the Er^{3+} ion in gold have been studied at low temperatures for reasons related to both the physics of the system and to its possible use in low temperature technology. The direct hyperfine transitions associated with the coupling of the Er^{167} nucleus to the 4f electrons has been observed in the 100 to 300 MHz frequency range in fields between 0 and 1000 gauss and at temperatures below $0.5^{\circ}K$. The hyperfine coupling constant A and the pseudonuclear g-factor have been accurately determined and provide an understanding of the crystalline field of the cubic Au host and the interaction of the localized 4f electrons of the Er with the conduction electrons of the metal. Linewidth and relaxation-time measurements have also been made and related with other studies and theory. The possible use of this system for absolute thermometry in the millikelvin temperature range has been shown to be limited by lineshape and intensity considerations.

Principal Investigator: G. Seidel (Physics)

Personnel: M. Sjöstrand (Physics)

Publications: Sjöstrand, M., and Seidel, G., "Hyperfine Resonance Properties of Er^{3+} in Au," Phys. Rev., in press.

Supported by the National Science Foundation.

Thermodynamic Properties of Helium below $1^{\circ}K$

By using a superconducting cavity with an extreme high quality factor we have been able to complete several different experiments on the properties of helium between 80 and $600^{\circ}mK$. The frequency of the cavity can be measured to an accuracy approaching 1 part in 10^{11} and can therefore be used through the Clausius-Massotti relation to measure the density of a dielectric material within it. Two experiments have been successfully completed and several others are still under active study. These include:

(i) the thermal expansion of liquid He^4 has been measured with two orders of magnitude better precision than previously. Deviations from a T^3 temperature dependence are observed below $0.5^{\circ}K$ and correlated with the anomalous curvature of the dispersion relation of phonons at low momentum;

(ii) the temperature dependence of dP/dT along the liquid-solid coexistence curve has been precisely determined, and through the Clausius-Clayperon relation the heat capacity of solid is found to be strictly T^3. The unusual behavior of the heat capacity reported by others is not observed;

(iii) the thermal expansion of dilute solutions of He^3 in He^4 has yielded information concerning the pressure dependence of the effective mass of the quasiparticles and a measure of the deviations of the parabolicity of their dispersion relations.

Principal Investigators: H. Maris (Physics)
G. Seidel (Physics)

Personnel: J. Berthold (Physics), N. Hanson (Physics), and L. Nagurney (Physics)

Publications: in prepartion.

Supported by the National Science Foundation.

Phonon-Phonon Interaction in Liquid Helium

Studies of the propagation of ultrasonic waves in liquid helium four continue. The purpose of this investigation is to relate phonon-phonon scattering characteristics with the phonon dispersion relation. The temperature range covered in these experiments is 50 mK $\gtrsim$ 400 mK. Special attention is given to the relative changes in ultrasonic velocity $(\frac{\Delta v}{v})$ as a function of frequency, since the sign and magnitude of the rate of change of $(\frac{\Delta v}{v})$ with frequency depend on the nature of the phonon dispersion relation for small wave vector phonons. The results obtained to date on velocity changes at saturated vapor pressure are consistent with "positive" dispersion (e.e, increasing velocity with increasing energy). This research is being extended to higher pressures.

Principal Investigator: C. Elbaum (Physics and Applied Mathematics)

Personnel: W. Junker (Physics)

Publications: None

Supported by the National Science Foundation.

Heat Pulses and Phonon Transport in Solids

Studies of propagation of short duration heat pulses and of phonon transport continue. The current emphasis is on determining the scattering of high frequency phonons (heat pulses) by static imperfections and by moving dislocations. The latter is accomplished by simultaneous propagation of heat pulses and ultrasonic waves. The configurations selected for this purpose are such that the ultrasonic waves couple to movable dislocations, but no coupling is expected between the ultrasonic waves and the phonons generated by the heat pulse. These studies are being carried out primarily on alkali halides. The aim of this study is twofold: To determine the effect of dislocation-phonon interactions on the drag experiences by dislocations moving through a crystalline lattice; 2) The determination of phonon scattering by moving dislocations.

Principal Investigator: C. Elbaum (Physics and Applied Mathematics)

Personnel: A. Hikata (Applied Mathematics) and M. Rodriguez (Physics).

Publications: None

Supported by the National Science Foundation.

Studies of the Transmission of Phonons across Interfaces

We have made measurements of the transmission of phonons across interfaces between silicon crystals and various condensed gases using the heat-pulse reflection technique. Our earlier measurements had shown that while the transmission into solid neon was in reasonable agreement with the acoustic-mismatch theory, the transmission into liquid helium-4 was larger than expected by a factor of between 10 and 50. In addition, it was found that the transmission for transverse phonons was larger than for longitudinal phonons. The experiments conducted recently have been designed to find out whether the anomalous transmission is unique to liquid helium, or if it is a general feature of transmission into materials for which quantum effects are important. The following new results have been obtained:

(i) Measurements were made for liquid helium under pressure and for solid helium. The transmission coefficient was found to be essentially independent of pressure and within experimental error, there was no discontinuity at the solidification pressure. Preliminary measurements have been obtained for solid helium at a pressure of 200 atmospheres.

(ii) Measurements of the transmission into solid hydrogen and deuterium were made. These gave results which were quanlitatively similar to those found for helium. The transmission was roughly 5 or 10 times larger than expected from the acoustic mismatch theory.

These results indicate that anomalous transmission does indeed appear to be a general feature of an interface involving quantum systems.

Principal Investigator: H.J. Maris (Physics and the Metals Research Laboratory)

Personnel: J.D.N. Cheeke, Visiting Professor from the CNRS Grenoble and,
J. Buechner (Physics).

Publications: None

Supported by the National Science Foundation.

Summaries of Other Related Work

Dislocation Dynamics - C. Elbaum (Physics and Applied Mathematics) - See Section 1

Transition Metal Chemistry - A. Wold (Engineering and Chemistry) - See Section 5

Theoretical Studies of Condensed Electron-Hole Droplets in Semiconductors - T.L. Reinecke (Physics) - See Section 7

Two-Dimensional Plasmas - P.J. Stiles (Physics) - See Section 7

Resonance Studies on Several Polycrystalline Indium Thiospinels
E.A. DeMeo (Engineering) and G.S. Heller (Engineering)
See Section 13

SECTION 9

Pseudo-One-Dimensional Conductors

Resonance Raman Study of Electron Delocalization and Thermochromism in a Polydiacetylene

The Raman spectra of the polydiacetylene polymer poly-ETCD, of the form $[=C(R)-C\equiv C-C(R)=]_n$, formed by the solid state polymerization of $[RC\equiv C-C\equiv CR]$ where R is $-(CH_2)_4OCONHC_2H_5$, reveal dramatic chcanges in the frequency and intensity of the $\nu(C=C)$ and $\nu(C\equiv C)$ bands as a function of both source-frequency and temperature. The polymer undergoes a nearly reversible (green-red) thermochromic phase transition at ca 135°C. The spectral changes result from the thermal transition and from selective enhancement of vibrations for domains with whose electronic transitions the source is in resonance. The π-electron delocalization is thus shown by Resonance Raman spectroscopy to occur over segments, or domains, along the polymer backbone. The distribution of the "domain lengths" is peaked at three values at 25°C but at one value above the transition.

Principal Investigator: W. M. Risen, Jr. (Chemistry)

Personnel: G. J. Exarhos (Chemistry)

Publications: Exarhos, G. J., Risen, Jr., W. M., Baughman, R. H., "Resonance Raman Study of the Thermochromic Phase Transition of a Polydiacetylene," Am. Chem. Soc., in press (1975).

Supported by the National Science Foundation and the United States Office of Naval Research.

Pseudo One-Dimensional Conductors

Experimental interest in quasi one-dimensional systems has been stimulated by experiments on the organic crystal, TTF-TCNQ, the polymer $(SN)_x$ the platinum salts $K_2[Pt(CN)_4]\ Br_{0.30} \cdot 3H_20$ and by the Brown CdS result. We have been investigating the Luther-Peschel and Emery-Luther solutions of the Luttinger, Mattis-Lieb model of one-dimensional interacting fermions with a view toward generalizing the result of Luther and Emery to an extended range of values of the coupling constant. Earlier exact many-body results on a strong coupling model (Cooper and Stolan) have been applied to the above model yielding information on the analytic properties and spectrum of this one dimension system of interacting fermions. We believe that a wider solution in the strong coupling (very narrow band) case can be found. This then could be generalized to the model with linearized kinetic energy using Wilson's method for solving the Kondo problem.

Principal Investigator: L. N. Cooper (Physics)

Personnel: E. Berkcan (Physics)

Supported by the Advanced Research Projects Agency.

Pseudo-One Dimensional Conductivity in Plastically Deformed Compound-Semiconductors

Extraordinary anisotropy (10^8) and unusual temperature dependence of the electrical conductivity have been observed in plastically deformed CdS. These features are attributed to metallic-type conductivity along a pseudo-one-dimensional system consisting of arrays of dislocations. The observed temperature dependence of the conductivity is consistent with a Peierls-type metal-semiconductor transiton at 125 K.

Principal Investigator: C. Elbaum (Physics and Applied Mathematics)

Personnel: None

Publications: Elbaum, C., "Pseudo-One-Dimensional Conductor-Plastically Deformed CdS," Phys. Rev. Letters 32, 376 (1974).

Summaries of Other Related Work

Problems in Strong Interaction Physics - A. Houghton (Physics)
See Section 8

SECTION 10

General Studies of Mechanical Properties

Small Deformations of Highly Anisotropic Materials

A previously-reported paper on plane traction problems for ideal composites appeared in print (1).

A paper on the mathematical theory of linear constraint condtions in linear elasticity theory was prepared (2). This work is concerned with general inhomogeneous, anisotropic elasticity materials with a single linear, inhomogeneous constraint condition. It was shown that the standard mixed boundary value problem determines at most one displacement field, but that the stress field may be indeterminate to the extent of an arbitrary "purely reactive" stress field. If the stress field is indeterminate, the problem is illposed and non-existence of solutions can be expected. For use in such cases, a modified theory is proposed which makes use of a relaxed form of the constraint condition and allows existence of solutions.

Principal Investigator: A. C. Pipkin (Applied Mathematics)

Personnel: V. Sanchez (Engineering)

Publications: Pipkin, A. C. and Sanchez, V. M., "Existence of Solutions of Plane Traction Problems for Ideal Composites. SIAM J. APPL. MATH. 26, 213 (1974). (1)

Pipkin, A. C., "Constraints in Linearly Elastic Materials," J. Elast. submitted. (2).

Supported by the National Science Foundation.

Finite Deformations of Fiber-Reinforced Composites

Two previously reported papers appeared in print (1,2).

The problem of finite axisymmetric deformations without twist, for fiber-reinforced bodies with an axis of rotational symmetry, was studied (3). The fibers were taken to lie in meridianal planes, with the field of fiber directions solenoidal. The theory of ideal fiber-reinforced composites was used. It was shown that the kinematic constraint conditions of this theory determine the deformation uniquely, when the deformed shape of

one fiber and the location of one point on each fiber are given. The general problem was reduced to quadratures. Special problems involving tubes reinforced with axial fibers were solved explicitly, as examples.

Principal Investigator: A. C. Pipkin (Applied Mathematics)

Personnel: None

Publications: Pipkin, A. C., "Finite Deformations of Ideal Fiber-reinforced Composites. Composite Materials, vol. 2: Mechanics of Composite Materials, G. P. Sendecky, Editor. New York: Academic Press, 1974.

Pipkin, A. C., "Generalized Plane Deformations of Ideal Fiber-reinforced materials," Quart. Appl. Math. 32, 253 (1974).

Pipkin, A. C., "Finite Axisymmetric Deformations of Ideal Fibre-reinforced Composites. QJMAM. Forthcoming.

Supported by the National Science Foundation and the Advanced Research Projects Agency.

Effect of Diffusion of Gases During Creep of Plastics

To determine the effect of diffusion of gases during stressing on the creep of polymers, thin-walled tubular specimens are subjected to axial loads with simultaneous internal pressure resulting from the pressurized gas whose influence on diffusion is being investigated.

The effect of several gases has been evaluated for polycarbonate, and a report on this project has been completed.

Principal Investigator: W. N. Findley (Engineering)

Personnel: H. Hojo, Department of Chemical Engineering, Tokyo Institute of Technology, Japan.

Publications: Hojo, H., and Findley, W. N., "Effect of Gas Diffusion on Creep Behavior of Polycarbonate," Polymer Engineering and Science Vol. 13, No. 4, July 1973, pp. 255-265.

Supported by the National Science Foundation.

Thermal Expansion Instability in Plastics

The thermal expansion of some polymers has been found to be a transient phenomenon. During the transition following an increase in temperature the creep rate has been found to be much greater than after stabilization. Experiments were performed to find polymers which do not exhibit this behavior and to determine the cause.

Principal Investigator: W. N. Findley, (Engineering)

Personnel: R. Mark (Engineering) and R. M. Reed (Engineering)

Publications: Findley, W. N. and Reed, R. M.,"Thermal Expansion Instability and Effect on Creep of Polyurethane," Trans. Soc. of Rheology (in press).

Supported by the National Science Foundation.

Combined Stress Creep at Eleavated Termperatures

Objective: The objective of this study is to determine the influence of temperature on the creep of polymers and to develop suitable theories for variable temperature.

Approach: Experiments are being performed under combined tension and torsion at elevated temperatures on a polyurethane plastic and polyethylene in the nonlinear range under combinations of tension and torsion. Experiments under varying temperature have been performed to provide information on suitability of theory for variable temperature. It has been found that creep is temperature history independent during rising temperature, but temperature history dependent during falling temperature. Many experiments have been made on several plastics in which rising and falling temperature histories have been imposed during creep.

Principal Investigator: W. N. Findley (Engineering)

Personnel: R. Mark (Engineering) and R. M. Reed (Engineering)

Publications: Lai, J. S. Y., and Findley, W. N., "Creep of Polyurethane under Varying Temperature for Nonlinear Uniaxial Stress," Transactions of the Society of Rheology, Vol. 17, Issue 1, 1973, pp. 63-87.

Lai, J. S. Y., and Findley, W. N., "Elevated Temperature Creep of Polyurethane under Nonlinear Torsional Stress with Step Changes in Torque," Transactions of the Society of Rheology, Vol. 17, Issue 1, 1973, pp. 129-150.

Mark, R., and Findley, W. N., "Nonlinear Creep of Polyurethane under Combined Stresses and Elevated Temperatures," Trans. Soc. of Rheology, Vol. 18, Issue 4, 1974, pp. 563-582.

Mark, R. and Findley, W. N., "Temperature-History Dependence in Combined Tension-Torsion Creep of Polyurethane under Varying Temperature," Trans. Soc. of Rheology (in press).

Supported by the National Science Foundation.

Subsequent Yield Surfaces for Steel

Objective: To study the nature of the yield surface and subsequent yield surfaces for steel, combinations of tension, torsion, compression are applied to tubular specimens to determine the yield point under various combined stresses both before and after yielding.

Progress:

(i) The effect of plastic strain on the yield surface has been investigated for 304L stainless steel in quadrants 1 and 4 of axial stress-shear space.

(ii) Initial and subsequent yield surfaces for SAE 1017 annealed mild steel have been found in all four quadrants of σ, τ space. Both load and strain control tests were conducted. Information on upper and lower yield points, constrained flow tests, normality, convexity, ageing, corners, cross effects and Bauschinger effects is available.

(iii) Initial and subsequent yield surfaces tests for SAE 1018 cold drawn steel have been completed. Analysis is in progress.

Principal Investigator: W. N. Findley (Engineering)

Personnel: M. J. Michno, Jr., Assistant Professor, Department of Mechanical and Aerospace Engineering, Washington University, St. Louis, Missouri.

R. M. Reed (Engineering)

Publications: Michno, M. J., Jr., Findley, W. N., and Reed, R. M., "A Low Interaction Tension (or Compression) Torsion Load Cell," Review of Scientific Instruments Vol. 44, No. 8, August 1973, p. 1148.

Michno, M. J., Jr., and Findley, W. N., "An Historical Perspective of Yield Surface Investigations for Metals," International Journal of Nonlinear Mechanics (in press).

Michno, M. J., Jr., and Findley, "Experiments to Determine Small Offset Yield Surfaces for 304L Stainless Steel under Combined Tension and Torsion," Acta Mechanica Vol. 18 1973, pp. 163-179.

Michno, M. J., Jr., and Findley, W. N., "Subsequent Yield Surfaces for Annealed Mild Steel under Dead-weight Loading: Aging, Normality, Convexity, Corners, Bauschinger and Cross Effects," Journal of Engineering Materials and Technolgy Vol. 96, Ser. H. No. 1, Jan. 1974, pp. 56-64.

Michno, M. J., Jr., and Findley, W. N., "Subsequent Yield Surfaces for Annealed Mild Steel under Servo-Controlled Strain and Load Histories: Aging, Normality, Convexity, Corners, Bauschinger and Cross Effects," Trans. ASME, J. Engr. Matls. & Technology, Vol. 14, 1974, p. 724.

Supported by the National Science Foundation.

Multi-Integral Representative for Creep of Plastics

Approach: The biaxial creep of thin-walled tubes of polurethane resulting from axial tension (or compression) and internal pressure is being studied. The data from this series of experiments are being compared to prediction based on previous results of combined tension-torsion creep. Experiments under irregular loading histories have also been performed. Other methods of analysis have included a linear compressibility assumption and a limited memory assumption.

Progress: Experiments under axial compression and internal pressure and tension-torsion have been completed. Some of the data reduction has been completed. Additional experiments were performed to check earlier results. Analysis of data has continued.

Principal Investigator: W. N. Findley (Engineering)

Personnel: R. M. Reed (Engineering), J. F. Tracy (Engineering) and K. Onaran, Professor, Istanbul Technical University, Istanbul, Turkey.

Publications: Findley, W. N., and Onaran, K., "Incompressible and Linearly Compressible Viscoelastic Creep and Relaxation," Transations, American Society of Mechanical Engineers, Journal of Applied Mechanics Vol. 41, A1, Mar. 1974, pp. 243-248.

Findley, W. N., and Tracy, J. F., "16-Year Creep of Polyethylene and PVC," Polymer Engineering and Science Vol. 14, # 8, Aug. 1974, pp. 577-580.

Findley, W. N., and Reed, R. M., "An Extensometer for Circumferential Strain," ASTM Journal of Testing and Evaluation (in press).

Nolte, K. G. and Findley, W. N., "Approximation of Irregular Loading by Intervals of Constant Stress Rate to Predict Creep and Relaxation of Polyurethane by Three Integral Representation," Trans. Soc. of Rheology, Vol. 18 Issue 1, 1974, pp. 123-143.

Supported by the National Science Foundation.

Solid State Processes Affecting Creep

The ultimate objectives of this study were to relate the diffusion rates of critical diffusing species to the creep deformation in silicates such as feldspars and micas. The deformation studies during the past year were concentrated on potassium feldspar, no experimental deformation studies have previously been done on this material.

A number of constant strain rate deformation experiments were performed on single crystals cored from a non-perthitic microcline (Or_{98}) oriented with the core axis parallel to [012] and perpendicular to $\underline{a}$. The purpose of these was to ascertain roughly what range of temperature and stress would be appropriate for the creep experiments. Experiments at a confining pressure of 15 kb, a strain rate of 10^{-5}/sec, and

temperatures of 900, 1000, and 1100°C all showed a sharp yield point followed by steady state flow. The yield strengths were approximately 12, 6, and 4kb respectively. Thin sections of the samples showed deformation bands and severe undulatory extinction consistent with glide on (010) or (001). No deformation lamellae or recrystallization were observed in any of the samples. A number of these experimentally deformed crystals were examined using transmission electron microscopy, but unfortunately the original twinned substructure of the material made it difficult to identify features produced during deformation, and to characterize these in any detail.

Aggregates of pure potassium feldspar are not found in nature, and so must be prepared artificially. We first tried crushing and seiving a natural crystal of microcline, and hot-pressing these fragments at 15 kb and 1100°C We were successful in producing aggregates of theoretical density, starting with either 10 μm or 48-53 μm sizes, but because of the excellent cleavage of feldspar these aggregates had a strong crystallographic preferred orientation. In addition, they had the same initial microstructure as the single crystal experiments. We thus developed a technique for crystallizing aggregates from synthetic gels, at 15 kb and 800°C, then increasing the temperature to 1100°C to promote grain growth. This material has no initial substructure. In the future we would plan to crystallize a sample at these conditions <u>in situ</u> in the deformation apparatus, and then to turn the temperature to whatever was desired for the deformation and turn on the moter.

Diffusional aspects of this work centered on the development of a new method for measuring diffusion in crystals, where the innovation involved using an ion microprobe analyzer to measure the isotope ratio gradients established from a crystal surface inward as isotope exchange took place. This new method has marked advantages in silicate diffusion studies in that it permits determination of very low diffusion coefficients and it also permits measurement of diffusional anisotropies in crystals. The particular study carried out was for sodium in albite feldspar ($NaAlSi_3O_8$). A linear Arrhenius was obtained for the temperature range 800° to 500°C. The diffusion coefficient for transport perpendicular to the (001) face was ten times greater than that perpendicular to the (010) face at 800°C and 2000 bars pressure.

In sum, we have developed a number of techniques and done a number of preliminary experiments, showing that the original goals of the project are indeed feasible. Data on the self diffusion of K, Na and O in potassium feldspar have already been measured, and now we have a rough idea of the strength of this material.

Principal Investigators: B. J. Giletti (Geological Sciences) J. Tullis (Geological Sciences) and T. Tullis (Geological Sciences)

Personnel: None

Publications: Giletti, B. J., 1974, "Studies in Diffusion I: Argon in Phlogopite Mica," Proc. Conf. on Geochem, Transport and Kinetics, Hofmann, A, et al., eds., Carnegie Inst. of Washington, pub.

Giletti, B. J., 1974, "Diffusion Related to Geochronology," Proc. Conf. on Geochem. Transport and Kinetics, Hofmann, A. et al., eds., Carnegie Inst. Washington, pub.

Sipling, P. J., and Yund, R. A., 1974, "Kinetics of Al/Si Disordering in Alkali Feldspars," Proc. Conf. on Geochem. Transport and Kinetics, Hofmann, A. et al., eds., Carnegie Inst. of Washington, pub.

Tullis, J., "Elastic Strain Effects in Coherent Perthitic Feldspars," Contributions to Mineralogy and Petrology, v. 49, pp. 83-91.

Yund, R. A, 1974, "Coherent Exsolution in the Alkali Feldspars," Proc. Conf. on Geochem. Transport and Kinetics, Hofmann, A., et al., eds., Carnegie Inst. of Washington, pub.

Yund, R. A., and Anderson, T. F., "Oxygen Isotope Exchange Between Potassium Feldspar and KCl Solutions," Proc. Conf. on Geochem. Transport and Kinetics, Hofmann, A., et al., eds., Carnegie Inst. of Washington, pub.

Hofmann, A. W., Giletti, B. J., Anderson, C. A., Hinthorne, J. A., and Comaford, D., "Ion Microprobe Analysis of a Potassium Self-Diffusion Experiment in Biotite. Submitted to Earth and Planetary Science Letters.

Supported by the National Science Foundation.

Tensile Shock Waves in Rubber

When finite tensile pulses are propagated along stretched rubber filaments there is a tendency for the front of the pulse to become sharper and sharper until a tensile shock front is developed. This shock wave production is assoicated with the nature of the stress-strain curves

of rubber which is 'concave upwards'. This results in large tensile disturbances travelling at velocities very much higher than those of smaller amplitude with the consequent production of tensile shock fronts. The production of such tensile shock fronts is normally inhibited by the very high attenuation to wave propagation in rubber, and it is only at very high degrees of pre-stretch that these fronts can be observed. Experimental work on the formation of such fronts in rubber and other high polymers has been carried out during this past year and in addition the phenomena of compressive 'shock tails' in these materials has been observed. Thus if a rubber filament is stretched and a compressive pulse is propagated along it, the highest amplitudes in this compressive pulse travel at lower velocities than the rest of the pulse, this results in a compressive shock tail to the pulse rather than a tensile shock front. The work is being continued with rubber and filaments of various polymeric materials, e.g. nylon, polyethylene and polytetrafluorethylene.

This work was supported by the United State Army Research Office and the Advanced Research Projects Agency.

Principal Investigator: H. Kolsky (Applied Mathematics)

Personnel: S. Shih (Engineering)

Torsional Oscillations of Pre-Stretched Polymeric Cylinders

The torsional oscillations of specimens of stretched rubber and polyvinyl chloride have been carried out with the intention of studying how the theory of large elastic deformations can be applied to materials which show time dependent properties. It has been shown that whereas the behavior of polyvinyl chloride would appear to conform to the simple elastic treatment, the response of rubber at high strains indicates that structural changes occur, probably due to crystallization, as viscoelastic stress relaxation takes place. A paper describing these observations is in preparation. Mr. Rosen presented a thesis for the Sc.M. degree based on this work.

Principal Investigator: H. Kolsky (Applied Mathematics)
A. C. Pipkin (Applied Mathematics)

Personnel: J. J. Wong (Engineering), J. Rosen (Engineering)
R. Stanton (Applied Mathematics)

This work was supported by the United States Army Research Office and the Advanced Research Projects Agency.

Non-Linear Relaxing Waves and Oscillations

Further work has been carried out on non-linear waves and oscillations using variational methods and a number of advances have been made. For the linearized equation, general solution in terms of Laplace transforms are obtained and more explicit expressions for exponential kernels are given. An iteration scheme is established for general kernels. For positive kernels, the stability condition for the solution is explicitly established. The large time solution as well as the solution representing the main disturbance is also obtained. For the non-linear equation, the condition for shock formation is obtained for a special kernel and for cases where the non-linearity is weak.

Principal Investigator: D. Y. Hsieh, (Applied Mathematics)

Personnel: J. P. Lee (Engineering)

Publications: Hsieh, D. Y. and Lee, J. P., "Experimental Study of Pulse Propagation in Curved Elastic Rods," J. Acous. Soc., Vol. 54, No. 4, 1973, pp. 1052-1055.

Hsieh, D. Y., "Variational Methods and Nonlinear Forced Oscillations," J. Mathematical Phys., Vol. 16, No. 1975, pp. 275-280.

Supported by the Advanced Research Projects Agency.

SECTION 11

Materials for Solar Cells

Mechanical and Electrical Imperfection in Solar Cells

The purpose of this research is to improve the efficiency of photovoltaic (solar) cells. In presdent day cells, only about one half of the theoretically available electrical energy is produced from the sunlight incident upon the cells. This project is focused upon the materials problems associated with these reduced efficiencies. The influence of material composition and perfection upon the measured electrical parameters of the cells is assessed by a variety of experimental techniques. In particular, the electron-voltaic response in the scanning electron microscope, localized photovoltaic response to light of selected wavelengths, and direct observation of crystalline perfection by x-ray topographical methods are compared and correlated with each other to determine the causes of reduced efficiency in the cells. Facilities for these techniques are being constructed. The capabilities of the techniques have been demonstrated in silicon and GaAs solar cells and indicate the need for increased attention to the characterization and careful control of chemical homogeneity and crystalline perfecton throughout the crystal growth and processing schedule in present day cells.

In GaAs, in particular, the examination by x-ray topography of commercially available wafers show them to be filled with second phase particles which cause extensive damage to the crystalline perfection. These studies suggest very strongly that the state of crystalline perfection of GaAs wafers used for solar cell fabrication must be under better control if satisfactory devices are to be fabricated.

In commercially available silicon solar cells some correlation has been observed between regions of reduced photovoltaic response and regions of high mechanical defect densities. The electron voltaic response (i.e. the cell short circuit current under electron beam excitation) in the scanning electron microscope suggests a correlation between the areas of reduced response and the presence of dislocations in the p-n junction region. This work is continuing with emphasis on the localization of the characterization techniques to specific regions of

the crystals examined and, in particular, to determination of minority carrier lifetimes.

Principal Investigator: B. Roessler (Engineering) and J. J. Loferski (Engineering)

Personnel: W. Oates (Engineering), R. Kaul (Engineering) and M. Schreiner (Engineering)

Publications: Loferski, J. J., Roessler, B., Crisman, E. E., Chen, L. Y., and Kaul, R., "Methods of Improving the Efficiency of Photovoltaic Cells," Eights Semiannual Report, September 1, 1973-February 28, 1974, NASA Grant NGR-40-002-093 (also see seventh and ninth semiannual reports).

Supported by the National Science Foundation and the National Aeronautics and Space Administration.

Methods of Improving the Efficiency of Solar Cells

The objective of this program is to explore new designs of solar cells which could lead to higher efficiency solar energy conversion and/or to less expensive fabrication methods. Specifically we have been constructing solar cells from single crystal silicon which have their surface covered by a grating pattern of p/n junctions made by alloying Al into n-type silicon. The width of the Al stripes is about 5μ and the spacing is up to 200μ. Experiments were performed on the optimum alloying temperature which turned out to be about 600°C. Cells having an area up to 1cm^2 and various grating line spacings have been made. The maximum efficiency (measured under an Air Mass Zero solar spectrum simulator) observed to date on a 1cm^2 cell is somewhat below 8%. The short circuit current of this grating cell is comparable to that of a standard commercial Si cell but the open circuit voltage is lower; however there is no reason why higher voltages should not be attainable in the grating cells. More work is required. Work has begun on making grating cells on single crystals of GaAs. In this case, the starting material is n-GaAs; the grating pattern is made from zinc which is an acceptor in GaAs. Because the diffusion length of minority carriers in GaAs is considerably smaller than in Si, the spacing between grating lines must be substantially smaller and the grating lines cannot be narrower.

Principal Investigator: J. J. Loferski

Personnel: B. Roessler (Engineering), E. E. Crisman (Engineering), L. Y. Chen (Engineering), J. Walker (Engineering), R. Kaul (Engineering)

Publications: Loferski, J. J., Crisman, E. E., Chen, L. Y., and Armitage, W., "Feasibility of Increasing Efficiency of Solar Cells by Means of Grating Cells, Tenth IEEE Photovoltaic Specialists Conference, Palo Alto, California, November 1973.

Loferski, J. J., Roessler, B., Crisman, E. E., Kaul, R., Chen, L. Y., Walker, J., "Methods of Improving the Efficiency of Solar Cells," Brown University Reports, August 1973 and February 1974; Ninth and Tenth Semiannual Reports on NASA Grant NGR 40-002-093.

Supported by the National Aeronautics and Space Administration.

SECTION 12

Optical Properties

Theoretical Studies of Optical Pumping of Gases Leading Toward the Development of Far Infrared Tunable Lasers

By a proper consideration of kinetic models it has become possible to properly assess both inhomogeneous and rotational relaxation effects in gas lasers. In particular, a knowledge of the relaxational behavior of rotational states is necessary in the analysis of laser behavior in the far infrared. There is a distinct possibility of line tunable lasers in the far infrared operating on a series of rotational transitions. One purpose of this study is to develop the analytical tools that may serve as guidelines in the construction and analysis of such devices.

Principal Investigator: T. F. Morse

Publications: Healy, J. J., Cipolla, J. and Morse, T. F., "On the Role of the Branching Ratio in Problems of Radiative Transfer," J. Quant. Spectrosc. Rad. Transfer 13, 1219 (1973).

Healy, J. J. and Morse, T. F., "Theory of an Optically Pumped Gas Laser," J. Quant. Spectrosc. Rad. Transfer 13, 235 (1973).

Goela, J. S., "Inhomogeneous Broadening Effects in a Gas Flow Laser," M.Sc. Thesis, (won second prize in Northeastern Regional Competition of the A.S.M.E.).

Supported by the United States Air Force of Scientific Research, Mechanics Branch.

Two Photon Absorption in III V Crystals

The experiments of two photon absorption in single crystal GaAs and CdTe, using a pulsed Nd glass laser at 1.06 micron,

have been completed

An anisotropy in the angular dependence was measured, which increases somewhat with lowering of the temperature.

Reasonable, quantitative agreement was obtained between the experimental observations and a simple, three band theory developed by us. Two band terms determine mainly the average size of two photon absorption while three band terms explain the observed anisotropy.

Principal Investigator: H. J. Gerritsen (Physics)

Personnel: S. Bepko (Physics)

Publications: Bepko, S., "The Anisotropy of Two Photon Absorption in GaAs and CdTe," Phys. Review B15, (1975) in print.

Supported by the National Science Foundation

XPS Studies of Bonding Using Final State Interactions

X-ray photoemission spectroscopy (XPS) has long obtained qualitative and quantitative chemical information by allowing studies of valence band spectra and of the relatively small changes (about 1 to 3 eV) in compounds of elemental core level energies (i.e. chemical shifts). However, we have recently observed an effect in the XPS spectra of the fifth period and rare earth elements ($40 \lesssim Z \lesssim 70$) which is particularly dependent on the chemical environment and may promise a new and potentially more sensitive way to use XPS to study bonding.

Although the relationship between photoemission spectra and the initial state of the electron is usually emphasized, an extreme example of the importance of the final state is the 4p ($N_{2,3}$) level of the fifth and sixth period elements. Although the initial state is a doublet several eV wide, the XPS spectra from this level show a single peak which increases in width with atomic number Z. The 4p level width grows from 4 eV for Mo (Z=42) to 13 eV for Ag (Z=47) to 40 eV for Te (Z=52). But of more practical interest is that any particular element's 4p level width changes dramatically with chemical environment. For instance, in pure Cd (Z=48) the 4p level is 20 eV wide, while in CdO it is 10 eV wide. This variation is much larger than the chemical shifts in this compound which are used as a measure of the ionicity in compounds. Because of the large size of the final state effects that lead to the anomalous 4 p level spectra, the changes that occur with

chemical environment are correspondingly large. We hope to apply this to the study of bonding in some systems for which other methods have previously proven unsuccessful.

Principal Investigator: G. B. Fisher (Engineering)

Publications: Fisher, G. B., Shalvoy, R., and Estrup, P. J., "Extreme Broadening of the $N_{2,3}$ (4p) Level in Fifth Period Elements," Bull. Am. Phys. Soc. 19, 233 (1974).

Supported by the National Science Foundation and the United States Army Research Office, Durham (AROD)

Picosecond Laser Research

An Experimental study of the linear growth region of ultrashort pulse generation was made. The pulse duration of an average pulse in the mode locked pulse train was observed to depend on the time of appearance of the train after flashlamp maximum. The results appear to agree with Letokhov's theory.

Principal Investigator: H. J. Gerritsen (Physics)

Personnel: R. Sam (Physics)

Publications: Sam, R., "An Experimental Study of the Linear Growth Region of Ultrashort-Pulse Generation in a Mode-locked Nd:glass Laser," Appl. Phys. Letters 24, 631 (1974)

Sam, R., "Laser Damage of GaAs and ZnTe at 1.06 micron," Applied Optics 12, 878 (1973)

Supported by the Advanced Research Projects Agency.

SECTION 13

Magnetic Properties

Ultrasonic Studies of Antiferromagnetic and Nuclear Acoustic Resonances

The effects of external magnetic fields and of temperature on the ultrasonic antiferromagnetic resonance were studied experimentally near the Néel temperature of $RbMnF_3$. The results are in reasonable agreement with the predictions of the two and four-sublattice models for some of the modes studied, whereas for others discrepancies are found between theory and experiment. A zero field splitting of the resonance is observed.

The frequency-temperature relation for nuclear resonance of Mn^{55} has been studied in the antiferromagnetically ordered phase of $RbMnF_3$, using ultrasonic methods. For $T \lesssim 60^{\circ}K$ molecular-field theory and for $60^{\circ}K \lesssim T \lesssim T_N$. (Néel temperature $T_N = 83^{\circ}K$) a modified molecular-field theory is found to be consistent with the experimental results. Evidence is found for a strong effect of coupling between nuclear and electronic spin-wave modes in $RbMnF_3$ near T_N.

Principal Investigator: C. Elbaum (Physics and Applied Mathematics)

Personnel: T. Jimbo (Physics)

Publications: Jimbo, T. and Elbaum, C., "Temperature and Magnetic Field Dependence of Ultrasonic Antiferromagnetic Resonance in $RbMnF_3$ near T_N," Solid State Comm. 15, 123 (1974).

Jimbo, T. and Elbaum, C., "Mn^{55} Nuclear Acoustic Resonance in Antiferromagnetic $RbMnF_3$ near the Néel Temperatures," Phys. Rev. B10, 2131 (1974).

Supported by the National Science Foundation.

Resonance Studies on Several Polycrystalline Indium Thiospinels

Ternary and quaternary indium thiospinels, MIn_2S_4 (M=Mn, Fe, Co and Ni) and $MnInCrS_4$, have been investigated by means of centimeter and millimeter wave resonance techniques over a temperature range of 4.2-300°K in powdered samples. Resonance absorption was observed in $MnIn_2S_4$ and $MnInCrS_4$ but not in the other materials. It has been reported that $MnIn_2S_4$ is paramagnetic and $MnInCrS_4$ is antiferromagnetic (AFM) with a Neel temperature of 13°K. By means of the magnetic field sweep method, (i) the magnetic field dependence of the resonance frequency was measured at room (RM), liquid-nitrogen (LN) and liquid-helium (LHe) temperature, and (ii) the temperature dependence of the resonance field was studied at fixed frequencies. By means of the frequency sweep method, the zero-field resonance was examined at LHe temperature.

At RM and LN temperatures, paramagnetic resonance data showed that the effective spectroscopic splitting factors are 2.03 and 2.01 for $MnIn_2S_4$ and $MnInCrS_4$, respectively. The temperature dependence of the resonance at fixed frequencies showed the following characteristics. As the temperature was decreased from RM temperature, the resonance field remained constant at first, while the half-maximum linewidth gradually increased, and then shifted toward lower fields while the linewidth increased abruptly. The strength of the resonance absorption decreased down to a certain temperature - different for each material - below which the strength was nearly constant. This phenomenon is evidence of a magnetic transition in both substances. For $MnInCrS_4$, such a transition occurred at temperatures around its Neel temperature, 13°K, whereas for $MnIn_2S_4$, the results suggested that the material is AFM with a Neel temperature of about 6°K, in disagreement with a previous report based on DC susceptibility data. Susequently, new susceptibility measurements were performed and the data obtained confirmed the resonance result by indicating a Neel temperature of 4.9°K. Consequently, it was concluded that $MnIn_2S_4$ is antiferromagnetic below 4.9°K.

The antiferromagnetic resonance data of $MnIn_2S_4$ and $MnInCrS_4$ at LHe temperature were compared with four models of AFM: the uniaxial easy axis AFM, the easy plane AFM, the canted AFM, and the helical AFM. None of these models was by itself consistent with all of the resonance data for either material.

Principal Investigators: E. A. DeMeo (Engineering) and G. S. Heller (Engineering)

Personnel: C. Hsu (Engineering)

Publications: Hsu, C., Steger, J. J., DeMeo, E. A. Wold, A., and Heller, G. S., "Magnetic Susceptibility of $MnIn_2S_4$", to be published in the Journal of Solid State Chemistry.

Supported by the National Science Foundation.

Lecturers in the Materials Research Laboratory Program, 1973-74

September 17, 1973

Solid Mechanics Seminar: Professor M. J. Randall, Department of Geological Sciences, Brown University, SEISMIC RADIATION FROM A CIRCULAR DISLOCATION.

September 20, 1973

Materials Science and Solid Mechanics Seminar: Professor J. P. Hirth, Department of Metallurgical Engineering, Ohio State University, GRAIN BOUNDARY STRUCTURE AND DISLOCATIONS.

September 24, 1973

Solid Mechanics Seminar: Dr. Alex Mackenzie, Department of Mechanical Engineering, The University, Glasgow, SOME EXPERIMENTAL RESULTS ON DUCTILE FRACTURE INITIATION.

September 27, 1973

Solid State Seminar: Professor See-Chen Ying, Physics Department, Brown University, HYDRODYNAMIC RESPONSE OF METALLIC SURFACES.

October 1, 1973

Physics Colloquia: Professor M. Tinkham, Department of Physics, Harvard University, FLUCTUATIONS AND RESISTANCE IN SUPERCONDUCTORS.

October 3, 1973

Joint Electrical Sciences and Solid State Seminar: Dr. Ryogo Hirota, Department of Mathematics and Physics, Ritsumeikan University, Kyoto, Japan, SOLITONS: THEIR PROPERTIES & APPLICATIONS.

October 4, 1973

Solid State Seminar: Dr. Truman Brown, Bell Telephone Lab, Murray Hill, New Jersey, SURFACE STATE ELECTRONS OUTSIDE OF LIQUID HELIUM.

October 11, 1973

Solid State Seminar: Dr. Y. C. Cheng, Bell Northern Research, THE INFLUENCE OF SURFACE ON HOLE MOBILITY IN METAL-OXIDE-SILICON STRUCTURE.

Lecturers in the Materials Research Laboratory Program, 1973-74

October 12, 1973

Chemistry Department Colloquia: Professor Jan Tauc, Division of Engineering and Physics Department, Brown University, STRUCTURE AND VIBRATIONAL SPECTRA OF AMORPHOUS SEMI-CONDUCTORS.

October 25, 1973

Solid State Seminar: Dr. William Brinkman, Bell Telephone Lab, Murray Hill, New Jersey, THE THEORY OF SUPERFLUID HELIUM - 3.

October 29, 1973

Solid Mechanics Seminar: Dr. C. F. Shih, Division of Engineering and Applied Physics, Harvard University, SMALL SCALE YIELDING ANALYSIS OF MIXED-MODE CRACK PROBLEMS.

November 1, 1973

Solid State Seminar: Dr. J. A. Van Vechten, Bell Telephone Lab, Murray Hill, New Jersey, LATTICE DEFECTS IN TETRAHEDRAL SEMICONDUCTORS.

Geological Sciences Seminar: Dr. D. L. Turcotte, Department of Geological Sciences, Cornell University, MEMBRANE AND THERMAL STRESSES IN THE LITHOSPHERE AND THEIR GEOLOGICAL IMPLICATIONS.

November 2, 1973

Center for Fluid Dynamics Colloquium: Professor S. Harris, Department of Mechanics, S.U.N.Y. at Stony Brook, COAGULATION IN AEROSOLS.

November 7, 1973

Materials Research Laboratory Discussion Group on Fracture: Professor Richard W. Hertzberg of the Department of Metallurgy and Materials Science, Lehigh University, FATIGUE FAILURE IN POLYMERS.

November 8, 1973

Geological Sciences Seminar: Dr. James Kirkpatrick, Hoffman Laboratory, Harvard University, KINETICS OF CRYSTALLIZATION IN THE SYSTEM $CaMgSi_2O_6$, $CaAl_2SiO_6$.

Lecturers in the Materials Research Laboratory Program, 1973-74

November 15, 1973

Solid State Seminar: Dr. Peter Yu, I.B.M., RESONANT RAMAN STUDIES IN SEMICONDUCTORS.

November 16, 1973

Center for Fluid Dynamics Seminar: Professor George Springer, University of Michigan, PARTICULATE EMISSIONS FROM AUTOMOTIVE ENGINES.

Materials Research Laboratory Group on Fracture: Dr. Leo Van Swam, Division of Engineering, Brown University, FATIGUE BEHAVIOR OF MARAGING STEEL.

Solid State Seminar: Dr. P. A. Penz, Texas Instruments, Dallas, Texas, HYDROPTIC EFFECTS IN LIQUID CRYSTALS.

November 19, 1973

Solid Mechanics Seminar: Professor J. Klepaczko, Institute for Fundamental Technological Research, Warsaw and the Division of Engineering, Brown University, SOME EXPERIMENTAL INVESTIGATIONS OF INCREMENTAL WAVE PROPAGATION IN BARS.

November 26, 1973

Solid Mechanics Seminar: Professor Paul S. Symonds, Division of Engineering, Brown University, DISPLACEMENT BOUNDS FOR LARGE PLASTIC DEFLECTIONS OF RATE-SENSITIVE STRUCTURES.

November 27, 1973

Chemistry Department Colloquia: Professor C. Austen Angell, Purdue University, SUPERCOOLED LIQUIDS, REAL AND SIMULATED.

November 29, 1973

Solid State Seminar: Dr. Bruce Patton, M.I.T., THE PEIERLS' INSTABILITY IN QUASI ONE-DIMENSIONAL ORGANO-METALLIC SYSTEMS.

December 3, 1973

Chemistry Department Colloquia: John F. Endicott, Wayne State University, PHOTOREACTION MODES IN COMPLEXES WITH nd^6 METALS.

Solid Mechanics Seminar: Professor Pin Tong, Department of Applied Mechanics and Engineering Sciences, University of California, San Diego, A HYBRID FINITE-ELEMENT APPROACH TO PROBLEMS IN ELASTICITY.

Lecturers in the Materials Research Laboratory Program, 1973-74

December 3, 1973 (cont)

Physics Colloquia: Professor Richard Ferrell, Department of Physics, University of Maryland, FIELD THEORY MODELS FOR PHASE TRANSITIONS.

December 5, 1973

Materials Science and Solid Mechanics Seminar: Dr. Thomas Surek, Division of Engineering and Applied Physics, Harvard University, THERMALLY ACTIVATED GLIDE IN THE PLASTIC DEFORMATION OF CRYSTALLINE SOLIDS.

December 6, 1973

Geological Sciences Seminar: Dr. Tony Gow, U. S. Army Terrestrial Sciences Center C R E L L, THE INTERNAL STRUCTURE OF THE ANTARCTIC ICE SHEET AS REVEALED BY DEEP CORE DRILLING.

December 7, 1973

Chemistry Department Colloquia: Thomas B. Reed, Lincoln Laboratory, Massachusetts Institute of Technology, PITFALLS, DETOURS, AND SHORTCUTS ON THE ROAD TO SINGLE CRYSTAL GROWTH.

December 10, 1973

Solid Mechanics Seminar: Dr. H. D. Hibbitt (MARC Analysis Research Corp., Providence, NON-LINEAR ANALYSIS OF PIPING ELBOWS.

December 14, 1973

Chemistry Department Colloquia: Professor Steven D. Colson, Yale University, THE COUPLING OF PHONONS TO ELECTRONIC TRANSITIONS IN MOLECULAR CRYSTALS.

January 9, 1974

Solid Mechanics and Materials Science Seminar: Dr. Y. M. Gupta, Department of Physics, Washington State University, SHOCK WAVE PROPAGATION IN LITHIUM FLUORIDE SINGLE CRYSTALS.

January 11, 1974

Materials Research Laboratory Discussion Group on Fracture: Dr. Thomas A. Cruse, Engineering Department, Pratt & Whitney Aircraft Division, United Aircraft Corporation, BOUNDARY INTEGRAL EQUATION SOLUTIONS FOR TWO- AND THREE DIMENSIONAL ELASTIC CRACK PROBLEMS.

Lecturers in the Materials Research Laboratory Program, 1973-74

January 11, 1974

Geological Sciences Seminar: Dr. M. J. Randall, Department of Geological Sciences, Brown University, THEORIES OF SEISMIC SPECTRA.

January 31, 1974

Joint Engineering and Solid State Physics Seminar: Dr. V. S. Vavilov (P. N. Lebedev Physics Institute, Moscow), SEMICONDUCTOR RESEARCH TOPICS AT P. N. LEBEDEVE PHYSICS INSTITUTE, MOSCOW, USSR.

February 7, 1974

Geological Sciences Seminar: Dr. Karlis Muehlenbachs, Geophysical Laboratory, Washington, D. C., THE OXYGEN ISOTOPE RATIOS IN ICELANDIC ROCKS: THEIR VARIATION IN NATURE AND THEIR SUSCEPTIBILITY TO CHANGE IN THE LABORATORY.

Solid State Seminar: Professor Humphrey J. Maris, Department of Physics, Brown University, THE DISPERSION CURVE OF SUPERFLUID HELIUM.

February 8, 1974

Chemistry Department Colloquia: Professor Robert L. Fulton, Florida State University, THE OPTICAL PROPERTIES OF A GUEST MOLECULE IN, AND THE DIELECTRIC PROPERTIES OF, A DISCRETE LATTICE.

February 14, 1974

Solid State Seminar: Dr. David Bartley, Department of Physics, Brown University, LARGE MOMENTUM EXCITATIONS IN ^{3}HELIUM - ^{4}HELIUM SOLUTIONS.

February 15, 1975

Chemistry Department Colloquia: Dr. Roger J. Araujo, Corning Glass Works, A DIFFUSION MODEL FOR THE BLEACHING OF PHOTOCHROMIC GLASS.

February 18, 1975

Solid Mechanics Seminar: Dr. U S. Lindholm, Department of Materials Sciences, Southwest Research Institute, San Antonio, STRENGTH PROPERTIES OF BRITTLE MATERIALS UNDER MULTI-AXIAL LOADING.

Lecturers in the Materials Research Laboratory Program, 1973-74

February 21, 1974

Solid State Seminar: Professor Robert Guyer, Department of Physics, University of Massachusetts, Amherst, SOLID ^{3}He : THERMODYNAMICS

February 22, 1974

Chemistry Department Colloquia: Professor Mitchell A. Winnik, University of Toronto, CONFIRMATIONAL ANALYSIS OF LONG HYDROCARBON CHAINS.

February 25, 1974

Physics Colloquia: Dr. R. P. Messmer, General Electric Research Center, Schenechtady, New York, MOLECULAR OREITALS, METAL CLUSTERS AND SURFACE SCIENCE.

February 27, 1974

Materials Research Laboratory Discussion Group on Fracture: Professor N. J. Grant, Director, Materials Science Center, Department of Metallurgy and Materials Science, Massachusetts Institute of Technology, FAILURE OF METALS AT ELEVATED TEMPERATURES.

February 28, 1974

Solid State Seminar: Dr. Robert Laibowitz, IBM Thomas J. Watson Research Center, SUPERCONDUCTING WEAK LINKS: MICROBRIDGES.

Geological Sciences Seminar: Dr. E. G. Bombolakis, Department of Geology & Geophysics, Boston College, THE FRACTURE PROCESS OF CRYSTALLINE ROCK.

March 11, 1974

Physics Colloquia: Professor E. W. Plummer, Department of Physics, University of Pennsylvania, ELECTRON SPECTROSCOPY OF SOLID SURFACES.

March 18, 1974

Solid Mechanics Seminar: Mr. M. G. Srinivasan, Department of Materials Engineering, University of Illinois at Chicago Circle, INITIATION OF ELASTIC-PLASTIC BOUNDARIES DUE TO LOADING AT SPHERICAL AND CYLINDRICAL CAVITIES.

Lecturers in the Materials Research Laboratory Program, 1973-74

March 25, 1974

Solid Mechanics Seminar: Professor Norman Jones, Department of Ocean Engineering, Massachusetts Institute of Technology, DYNAMIC PLASTIC RESPONSE OF STRUCTURES.

March 28, 1974

Solid Mechanics Seminar: Professor W. Prager, Savognin, Switzerland, and formerly Division of Applied Mathematics and Engineering, Brown University, METHODS OF STRUCTURAL OPTIMIZATION.

April 2, 1974

Solid Mechanics Seminar: Dr. John R. Lehner, Department of Engineering Mechanics, University of Pennsylvania and Spring Garden College, Philadelphia, RATE EQUATION APPROACH TO STATIC AND DYNAMIC FINITE DEFLECTION PROBLEMS.

April 4, 1974

Solid State Seminar: Dr. D. Hamann, Bell Laboratory, Murray Hill, New Jersey, ELECTRONIC STRUCTURE OF SEMICONDUCTOR SURFACES.

April 11, 1974

Geological Sciences Seminar: Dr. Dieter Stoffler, University of Tubingen, West Germany, DISTRIBUTION AND PROPERTIES OF EJECTA DEPOSITS OF EXPERIMENTAL AND NATURAL IMPACT CRATERS.

Solid State Seminar: Dr. D. Rainer, Institute fur Festkorperforschung, KFA, Julich and Cornell University, BOUNDARY AND SIZE EFFECTS IN SUPERFLUID H_e^3.

April 15, 1974

Solid Mechanics Seminar: Professor L. B. Freund, Division of Engineering, Brown University, SOME GENERAL RESULTS ON ELASTODYNAMIC SOLUTIONS FOR RUNNING CRACKS.

April 17, 1974

Materials Research Laboratory Discussion Group on Fracture: Professor Paul C. Paris, Division of Engineering, Brown University, SOME RECENT WORK ON FATIGUE CRACK GROWTH.

Lecturers in the Materials Research Laboratory Program, 1973-74

April 18, 1974

Solid State Seminar: Dr. J. Noolandi, Bell Telephone Laboratory, Homdel, New Jersey, THEORY OF STRUCTURAL PHASE TRANSFORMATION OF A-15 COMPOUNDS.

Chemistry Department Colloquia: Dr. Rudolf J. H. Voorhoeve, Bell Telephone Laboratories, CATALYTIC CONVERSION OF CO AND NO ON PEROVSKITE.

April 22, 1974

Solid Mechanics Seminar: Professor Bertile Storakers, Department of Strength of Materials, Royal Institute of Technology, Stockholm and Division of Engineering and Applied Science, Yale University, SOME ASPECTS OF UNIQUENESS AND STABILITY AT FINITE DEFORMATION FOR INELASTIC SOLIDS.

April 25, 1975

Solid State Seminar: Dr. B. I. Lundquist, Cornell University and Chalmers Technical University, Goteborg, Sweden, EXHCANGE AND CORRELATION IN ATOMS, MOLECULES AND METALS BY THE SPIN-DENSITY-FUNCTIONAL SCHEME.

April 29, 1974

Physics Colloquia: Professor Alan Luther, Department of Physics, Harvard University, QUANTUM FLUCTUATIONS IN ONE-DIMENSIONAL SUPERCONDUCTORS.

May 2, 1974

Solid State Seminar: Dr. Gunther Ahlers, Bell Lab., Murray Hill, New Jersey, EXPERIMENTS NEAR THE SUPERFLUID TRANSITION IN He^4 AND He^3 - He^4 MIXTURES

Geological Sciences Colloquium: Dr. W. R. Eckelmann, Esso Products Research Company, THE ENERGY CRISIS.

May 3, 1974

Chemistry Department Colloquia: Professor Robert Burwell, Northwestern University, STERIC INTERACTIONS ON CATALYST SURFACES.

Center for Fluid Dynamics Colloquium: Professor James C. Keck, Department of Mechanical Engineering, Massachusetts Institute of Technology, THE INSIDE STORY OF AUTOMOBILE AIR POLLUTION.

Lecturers in the Materials Research Laboratory Program, 1973-74

May 6, 1974

Materials Science/Solid Mechanics Seminar: Professor Morris Cohen, Department of Metallurgy and Materials Science, M. I. T., HIGH VOLTAGE MICROSCOPY APPLIED TO STUDIES OF STRAIN HARDENING.

May 8, 1974

Materials Research Laboratory Discussion Group on Fracture: Professor J. W. Hutchinson, Division of Engineering and Applied Physics, Harvard University, ASPECTS OF QUASI-STATIC CRACK GROWTH.

May 9, 1974

Geological Sciences Colloquium: Professor James W. Skehan, S. J., Department of Geology and Geophysics, Bosto.. College, THE COLLISION BOUNDARY BETWEEN THE PALEO-AMERICAN AND PALEO-EU-AFRICAN PLATES IN NEW ENGLAND.

Solid State Seminar: Dr. T. D. Schultz, IBM, PEIERLS' INSTABILITIES, SLIDING CONDUCTICITY AND INTERCHAIN EFFECTS IN QUASI-ONE-DIMENSIONAL SOLIDS.

May 10, 1974

Chemistry Department Colloquia: Dr. John D. Hoffman, National Bureau of Standards, CHAIN FOLDING IN POLYMER CRYSTALS.

May 13, 1974

Solid Mechanics Seminar: Professor J. D. Achenback, Northwestern University Technical Institute, ELASTODYNAMIC STRESS INTENSITY FACTORS FOR A BIFURCATING CRACK.

MATERIALS RESEARCH LABORATORY

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M.C. Yalabik	Fellow
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Index, Principal Investigators